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THE DISTRIBUTION OF NATURAL AND ANTHROPOGENIC ELEMENTS AND COMPOUNDS IN PRECIPITATION ACROSS THE U. S.: THEORY AND QUANTITATIVE MODELS

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ERRATA SHEET

In order to more clearly define the sources of support for this study, we need to change the wording of the following source identifications:

1. On the title page, footnote 1, credit must be given to the Department of Environmental Science and Engineering in the School of Public Health.

2. In the preface on page iv, 2nd paragraph, credit is given to the Environmental Research Division of the EPA. The correct title of this division is the Ecological Research Division, the same division that is responsible for the distribution of this booklet.

THE DISTRIBUTION OF NATURAL AND ANTHROPOGENIC ELEMENTS AND COMPOUNDS IN PRECIPITATION ACROSS THE U.S.: THEORY AND QUANTITATIVE MODELS.[1]

by Thomas G. Wolaver[2]

under the direction of
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Chapel Hill.

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October 1972

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PREFACE

The investigation presented here was initiated for two reasons:

(1) The International Biological Program needs as much background data as possible for its biome-wide and interbiome modeling activities. The mineral nutrients and pollutants contained in rainwater comprise an important input in natural and managed ecosystems. It is therefore important to the IBP that we evaluate the available literature. The heavy reliance on modeling of ecosystem processes and interactions has led to a need for rapid and versatile modeling methods. A study of chemical concentration in rainwater as it varies across the U.S. provides an opportunity to combine spatial modeling concepts with functional ecosystem modeling. The resulting contour maps show the behavior of the dependent variable over a geographical area. Such maps may be compared easily with maps showing variations of other environmental parameters over the same geographical area, and may stimulate discussion of possible relationships among the many environmental forces.

(2) Spatial modeling techniques will be essential to evaluate data from the proposed global environmental monitoring network. It was during one of the early planning meetings, in cooperation with the National Academy of Science, that we discussed with Mr. R. A. McCormick the possibility of using data from the National Precipitation Sampling Network for a modeling exercise.

We were very fortunate in finding in Tom Wolaver an interested and competent environmental sciences student, who has prepared this comprehensive evaluation of the NPSN data. Readers of this publication must realize that the data-set was rather limited with a spatial density of 33-35 stations for the entire U.S. Through enormous effort on the part of Mr. Wolaver, we were able to present many conclusions with a fair degree of confidence. We have driven the analyses to the furthest justifiable point, and in some cases they merely demonstrate the potential of the methods employed.

We certainly hope that the paper creates enough interest in the appropriate federal agencies to expand the National Precipitation Sampling Network. A federally maintained rural sampling network, with the addition of city and metropolitan stations wherever necessary and possibly operated by different

authorities, could greatly enhance our knowledge of wet fallout, rainout and washout patterns in time and space over the U.S.

We are grateful to the Environmental Protection Agency's Environmental Research Division for making possible the publication and distribution of this study.

HELMUT LIETH

Chapel Hill, N. C.
September 1972

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INTRODUCTION

Many investigators have observed the relationship between elemental concentration in and the quantity of precipitation (ERIKSSON 1952 & 1957, JUNGE 1963), but few have analyzed this relationship and its implications for rainwater chemistry. JUNGE (1963) and ERIKSSON (1952) have made fairly extensive observations on these parameters and have inferred that there is a negative exponential relationship between amount of rainfall and concentration of chemicals. Little progress has been made beyond determining the general function of the relationship. Only a few maps are available showing the precipitation chemistry pattern over larger continental areas. In view of present concern over air pollution, spatial models and display of chemicals in rainwater becomes increasingly important. This publication, therefore, attempts a contribution at three levels: 1) understanding the processes which are responsible for the negative exponential relationship between elemental concentration and precipitation, 2) attempting to quantify the negative exponential function for seven common elements and compounds, and 3) applying this information to produce computerized spatial displays (maps) of washout, rainout and total wet fallout patterns in the United States for Ca^{++}, K^{+}, Na^{+}, Cl^{-}, NH_4^{+}, NO_3^{-}, and SO_4^{--}.

THEORY OF WET FALLOUT

The negative exponential curve observed by JUNGE (1963) and ERIKSSON (1952) is in essence a composite of curves indicating the different forces at work in wet fallout processes. These are generally referred to as rainout and washout. Rainout is concerned with the processes of rainwater constituents within the clouds, while processes below the clouds are designated as washout. Figure . is a representative curve of the form $y = a \pm be^{\pm cx}$. This curve can be broken into two main sections. The vertical section of the curve (block A in Figure 1) represents the processes of washout and dilution as the amount of rainfall increases, washout encompassing the process of contact absorption for both gases and particulate matter, in addition to concentration by evaporation. The horizontal section (block B) approximates the rainout processes, in addition to dilution and washout. One would expect that as more rain was collected the initial input due to washout would be diluted and the concentration of materials due to rainout, especially material incorporated as condensation nuclei, would be approximated. For a discussion of the processes involved in

rainout and washout, see JUNGE (1963) and UNGEMACH (1969). It is interesting to note that the curve in Figure 1 is the same as that obtained if we plot concentration of chemicals versus amount of rainfall accumulated during a single storm (GEORGII & WEBER 1960). By using monthly values for precipitation and elemental concentrations, we conclude that we are simply summing the input or curves of individual storms.

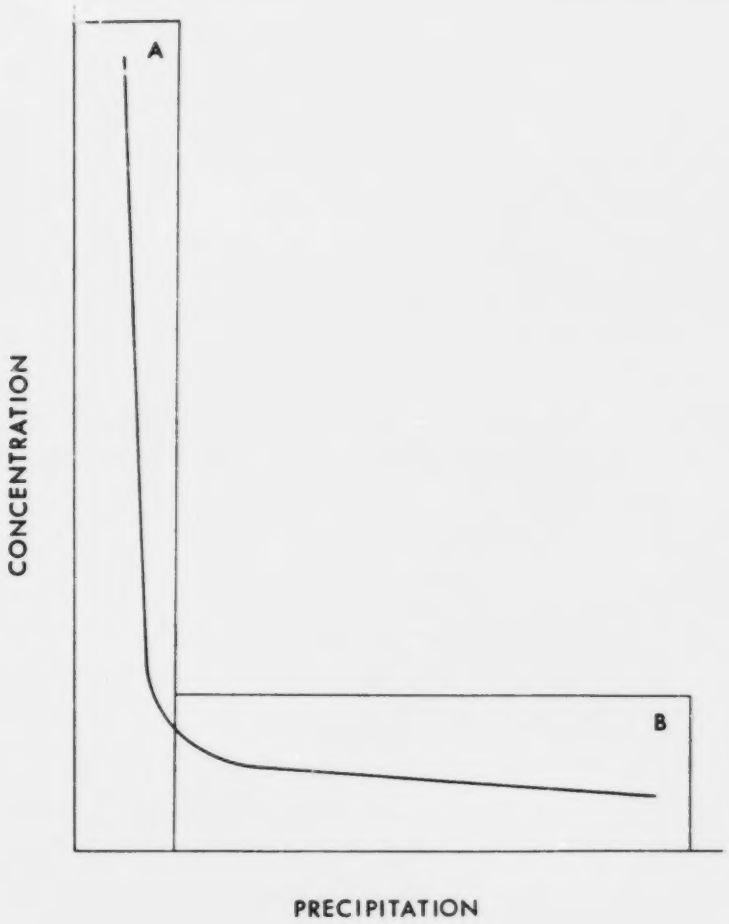


Figure 1. General form for the relation between chemical concentration and precipitation: $y = a \pm be^{\pm cx}$ (see eq. (1), next page)

Block A contains washout and dilution components. Block B contains rainout, washout and dilution components. With higher precipitation the washout component becomes insignificant.

METHODS

The data analyzed were collected in connection with the National Precipitation Sampling Network.[1] There were 33 stations scattered across the U.S., most of them in areas of urban concentration. The data encompassed the time period 1960-1964. Automated precipitation collectors remained open during periods of precipitation only, thus excluding dry fallout. A discussion of the collecting apparatus and methods of elemental analysis is presented by LODGE et al. (1968). Data from BEST (1971) and WELLS, WHIGHAM & LIETH (1972) were included where applicable. (A station list is included in Table VI.)

The sampling network data consisted of columns listing monthly concentrations of Ca^{++}, K^{+}, Na^{+}, Cl^{-}, NH_4^{+}, NO_3^{-} and SO_4^{--}, the monthly amount of precipitation, and the average pH of the rainfall.

For each of the seven chemicals, graphs were drawn of concentration versus amount of precipitation for all 33 stations. The form of the resulting curve for each station could be approximated by the equation

$$Y = U(1) \pm U(2)e^{\pm U(3)X} \qquad \text{eq. (1)}$$

where X = monthly rainfall amount,

Y = concentration in ppm, and

U(1), U(2), U(3) = constant coefficients.

The family of curves for this equation includes the negative exponential curve and the straight line.

Using the empirical data for Ca^{++}, K^{+}, Na^{+}, Cl^{-}, NH_4^{+} and NO_3^{-}, quantitative models of the relationship between concentration and precipitation were developed. The technique is demonstrated by using the element chlorine (Figures 2-4). Data for chlorine concentration was plotted against precipitation data for all stations for which enough information was available (see Table IV). When it was found that all these curves could be approximated by the general form of equation (1), groupings of curves were constructed by drawing a 45° line through the origin and dividing this line into three equal standard lengths, starting with the point at which the lowest curve intersected it. The standard length was selected arbitrarily. All the curves which crossed the 45° line within any of the three lengths were put into a group, and later were synthesized into one curve. Other chemicals fell into one and

---

[1] The original data assembled by the National Precipitation Sampling Network was provided through the courtesy of Dr. R. A. McCormick of the Environmental Protection Agency.

two groupings, such as K^+ and Na^+, respectively (see Figures 10 and 11). The synthesized curves were determined by running a nonlinear regression analysis on the data for all the curves which fell within the designated boundaries. For this procedure, a packaged program NONREG (QUADE 1970) was used.

The synthesized curves for chlorine are shown in Figures 2-4. The curve in Figure 2 indicates normal inputs of Cl^- with rainfall from 5 to 100 mm/month.

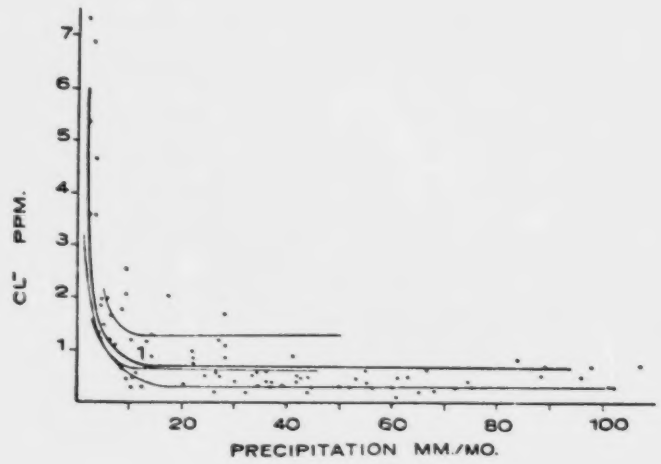


Figure 2. Synthesized chlorine curve 1, including bounding curves and data points. This curve represents natural input for this element.

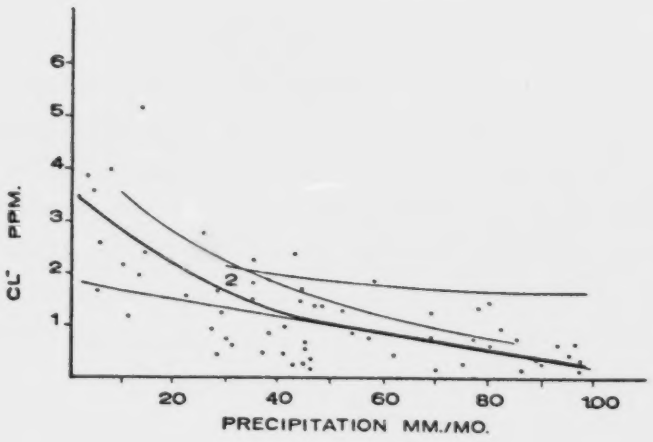


Figure 3. Synthesized chlorine curve 2, including bounding curves and data points. This curve represents very high anthropogenic input for this element.

The three curves in fine ink in this figure are nonlinear regression curves for three of the stations whose curves bounded the synthesized curve. Within their boundaries lie all the curves for the rest of the stations used in this synthesis. Figures 3 and 4 are the synthesized chlorine curves for areas of higher natural or anthropogenic pollution with their corresponding bounding curves. In Figures 3 and 4 the synthesized curves do not split the area within the bounding curves, likely due to excessive "noise" in some of the data.

One significant result of obtaining the quantitative relation of concentration to precipitation is the ability to differentiate between the processes of rainout and washout. A first approximation to rainout was calculated from an average of the two lowest values for monthly concentrations. Specifically, a value below the asymptote of the negative exponential should be picked because this asymptotic value depicts both rainout and washout. Washout concentrations

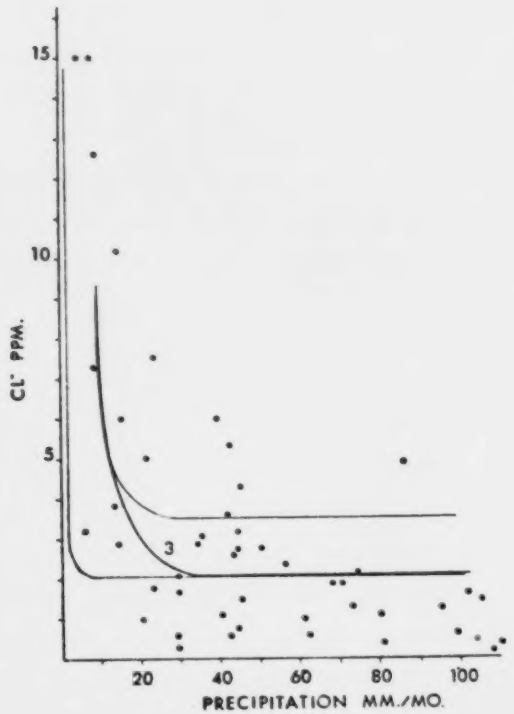


Figure 4. Synthesized chlorine curve 3, including bounding curves and data points. This curve represents very high anthropogenic input.

(ppm) were calculated by the following formula:

$$\text{average } C_w = \frac{\sum_{C=1}^{12} c_i P_i - \sum_{C=1}^{12} C_{ri} P_i}{\sum_{C=1}^{12} P_i} \qquad \text{eq. (2)}$$

where C_w = average washout concentration (ppm),

C_i = monthly chemical concentration (ppm),

P_i = monthly precipitation (mm), and

C_{ri} = monthly rainout concentration (ppm).

This data was further analyzed to determine what associations there might be between the investigated elements, compounds, and pH; especially, to determine if any of the chemicals are usually found together. This was accomplished with a program PARCOR (QUADE 1971), which calculates partial correlation coefficients between any two parameters. Pearson's R and Spearman's RHO were found for the chemical concentrations recorded at 14 selected stations, urban and rural (Table I). If Spearman's RHO is greater than .591, or if Pearson's R is greater than .497, a 95% level of confidence is achieved. Since the data used may not fit a normal distribution, the significance of Pearson's R coefficients is perhaps questionable. In addition, correlation coefficients are only measures of association and do not alone prove that two elements with a high correlation coefficient make up a compound supplying the individual constituents. In spite of these qualifications, most of the associations of importance have been used to infer which compounds supplied the elements recorded at the 14 stations.

Finally, maps of rainout concentration, washout concentration, and total wet fallout were produced for the chemicals discussed, using SYMAP (READER et al. 1972). SYMAP is a computerized mapping procedure that can be used to display quantitative data in a two-dimensional reference frame. The program processes data through several packages: A-OUTLINE, B-DATA POINTS, C-OTOLEGENDS, D-BARRIERS, E-VALUES, and F-MAP. The A-OUTLINE package was produced in this case by transferring a USA outline onto a grid, translating the outline into row-and-column coordinates, and punching the coordinates for each point at which the outline changes direction onto computer cards. The B-DATA POINTS package was produced by locating each of the 33 stations with row-and-column coordinates, and punching these coordinates on computer cards. To each of these B-DATA POINTS, E-VALUES (chemical concentration and total chemical fallout data from the Nation Precipitation Sampling Network) were assigned. SYMAP produces a contour map using a numerical interpolation routine based on the assumption that the influence of one data point upon another is inversely proportional to the square of the distance between the two points. For a detailed description of how to use SYMAP see READER et al. (1972) or DUDNIK (1972).

Table I. Partial correlation coefficients for element and compound pairs. For simplicity in reading table, valence signs have been omitted.

STATION	EVALUATED PAIRS	PEARSON'S R	SPEARMAN'S RHO
(95% confidence level when:		>.497	>.591)
Cape Hatteras, North Carolina	Ca, NO_3	.933	.150
	Na, Cl	.915	.628
	NH_4, SO_4	.748	.818
Philadelphia, Pennsylvania	Ca, Cl	.773	.003
	K, Na	.681	.637
	Na, Cl	.800	.814
Washington, D.C.	Ca, Cl	.665	.352
	Ca, NO_3	.533	.698
	K, Cl	.906	.393
	Na, Cl	.836	.549
Albany, New York	Ca, Cl	.680	.634
	Ca, NO_3	.774	.660
	Ca, SO_4	.787	.857
	Na, Cl	.938	.560
Chicago (O'Hare) Illinois	Ca, Na	.976	.642
	Ca, SO_4	.980	.792
	Na, Cl	.969	.673
Cincinnati, Ohio	Ca, Cl	.939	.801
	Ca, SO_4	.716	.727
	Na, Cl	.905	.390
Caribou, Maine	Ca, SO_4	.841	.018
Greenville, South Carolina	Na, Cl	.465	.491
	NH_4, NO_3	.870	.779
	pH, NO_3	-.839	-.957
Lake Charles, Louisiana	K, Na	.723	.628
	Na, Cl	.921	.948
	NH_4, NO_3	.503	.868
	pH, Ca	.847	.856
Amarillo, Texas	Ca, Cl	.848	.950
	Ca, K	.715	.958
	Ca, Na	.959	.928
	Ca, NO_3	.682	.567
	K, Cl	.949	.970
	Na, Cl	.945	.970
	Na, K	.819	.957
	pH, Cl	.493	.587
	pH, Na	.552	.615
	pH, SO_4	.715	.636
Grand Junction, Colorado	Ca, NH_4	-.639	-.815
	Ca, SO_4	.894	.906
	K, Cl	.943	.894
	K, Na	-.652	-.577
	Na, Cl	.853	.851
	pH, Na	.500	.834
Pocatello, Idaho	Ca, Cl	-.636	-.587
	Ca, SO_4	.655	.695
	K, NO_3	.819	.494
	Na, Cl	.931	.997
Glasgow, Montana	Ca, K	.652	.845
	Ca, SO_4	.440	.717
	K, Cl	.666	.795
	K, NH_4	.832	.446
	Na, Cl	.874	.933
	pH, Cl	.574	.555
	pH, Na	.529	.664
	pH, NO_3	-.588	-.640
Los Angeles, California	Ca, Cl	.645	.741
	Ca, SO_4	.775	.865
	Cl, NO_3	.764	.598
	K, Cl	.753	.679
	K, Na	.923	.817
	Na, Cl	.940	.879
	Na, NO_3	.882	.727

APPLICATION

Graphical Models of Concentration versus Precipitation

Using the theory presented above, concerning the relation between concentration and precipitation, and the curves drawn using data from the 33 stations, four graphical models (concentration versus precipitation) can be hypothesized that explain most of the variations of the general function on the basis of meteorological and physical differences. These are demonstrated in Figure 5. Table II summarizes the characteristics of the four models, A, B&C, D, and E.

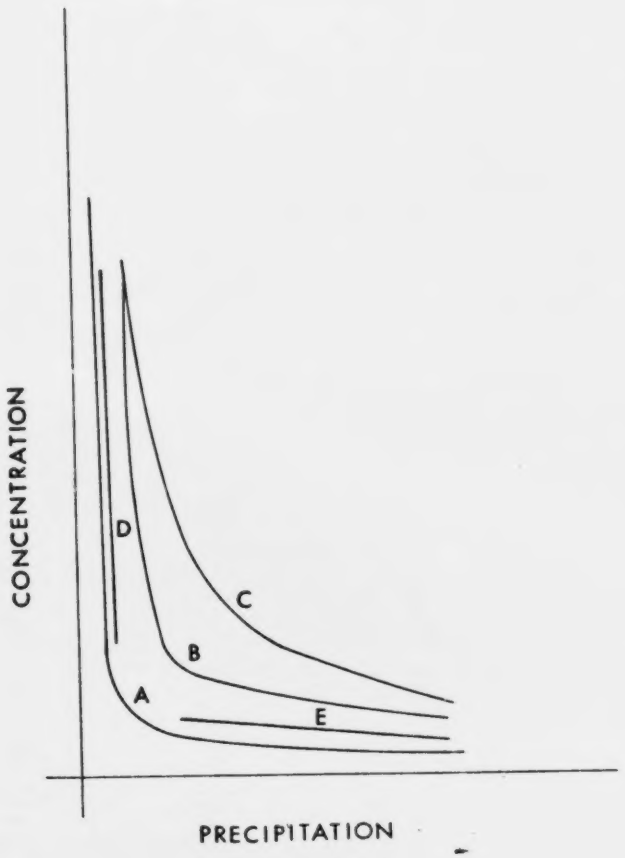


Figure 5. Graphical models of concentration vs precipitation, under hypothetical input conditions. Model A is for an area of "normal" input. Models B&C are for areas of high natural or anthropogenic pollution. Models D and E are the vertical and horizontal components of Model A, and exist under certain environmental conditions (see Table II).

Table II. General characteristics of the graphical models shown in Figure 5. All models were described by the general equation

$$Y = U(1) \pm U(2)e^{\pm U(3)X}$$

MODEL	CHARACTERISTICS	EXAMPLES
A	a) Both tails of curve defined. b) Inflection point well delineated. c) Variable ppt. d) $0 \leq \lvert U(3)\rvert \leq 1$, and $\lvert U(1)\rvert \leq 1$	Grand Island, Nebraska San Angelo, Texas
B&C	a) Both tails of curve defined. b) Inflection point less well defined; inflection point moves along the 45^{o} line. c) Variable ppt. d) As B approaches C, U(1) increases. As B or C approaches straight line, $U(3) \rightarrow 0$ and $\lvert U(2)\rvert \gg 1$; otherwise, $\lvert U(2)\rvert > 1$ and $U(3) < 0$.	Chicago, Illinois St. Louis, Missouri
D	a) Vertical component only. b) No inflection point. c) Dry, arid areas; monthly ppt. < 40 mm. d) Coefficients undetermined.	Nevada Montana Colorado
E	a) Horizontal component only. b) No inflection point. c) Extremely wet areas. d) $\lvert U(1)\rvert < 1$ and $U(3) \rightarrow 0$.	Tatoosh, Washington

Application of Quantitative Models to Concentration-vs-Precipitation Curves

Using equation (1) and the empirical data for Ca^{++}, K^{+}, Na^{+}, Cl^{-}, NH_4^{+}, and NO_3^{-}, quantitative models were derived which fit the graphical models. Sulfate ion was excluded due to its extremely erratic behavior in respect to precipitation. Figures 6-11 illustrate the different quantitative models that apply to each chemical. The actual equations and their implications are listed in Table III. Table IV lists the stations which were used to synthesize the general functions, with the exception of the functions for K^{+} and NH_4^{+}, for which all the stations were used.

The functions described in Table III can be used to quantify the input of Ca^{++}, K^{+}, Na^{+}, Cl^{-}, NH_4^{+}, and NO_3^{-} into ecosystems across the United States. Such application will yield an understanding of the atmospheric contribution of these elements and compounds in relation to the total rainfall. It should be pointed out that our data included only material that was incorporated through the processes of rainout and washout. Further study should incorporate the dry fallout factor when estimating the amount of chemical input in a given system. It may be that wet fallout data is sufficient in areas where stable air strata may lessen the contribution of dry fallout, but dry fallout would probably be a major factor in dry areas and/or areas with turbulent or downward-moving air masses.

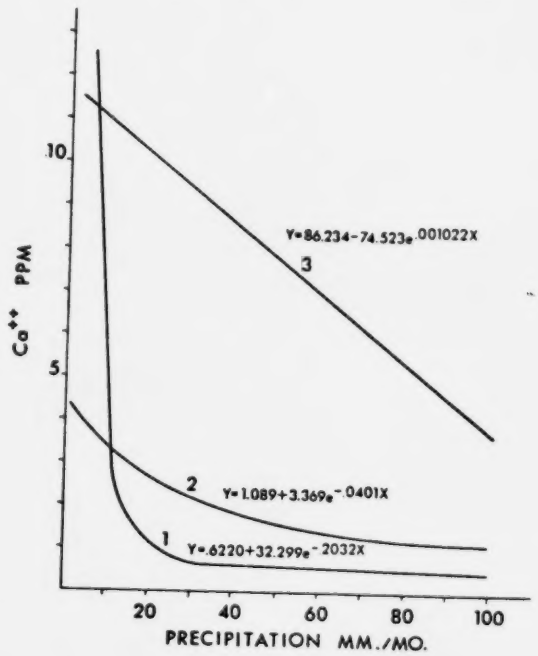


Figure 6. Quantitative models for Ca^{++}, showing pattern of graphical models A and B&C. Inputs are of natural and anthropogenic origin. Curves 2 and 3 reveal high concentration sources, natural or urban.

Table III. Quantitative models of concentration vs precipitation for the elements and compounds, excluding SO_4^{--}, and their implications.

ELEMENT OR COMPOUND	FIGURE, CURVE	GRAPHICAL MODEL	QUANTITATIVE MODEL	IMPLICATIONS
Ca^{++}	6,1	A	$Y=.6220+32.299e^{-.2032X}$	Natural sources.
	6,2	B&C	$Y=1.089+3.369e^{-.0401X}$	High concentration source, natural or urban.
	6,3	B&C	$Y=86.234-74.523e^{.001022X}$	
K^{+}	7	A	$Y=.2375+2.687e^{-.3039X}$	Natural sources.
Na^{+}	8,1	A	$Y=.4003+6.079e^{-.3106X}$	Natural sources.
	8,2	B	$Y=.9943+28.769e^{-.2277X}$	High concentration source, natural.
Cl^{-}	9,1	A	$Y=.6732+18.1872e^{-.6055X}$	Natural sources.
	9,2	B&C	$Y=.4673+3.1471e^{-.0338X}$	High concentration sources, natural and urban.
	9,3	B&C	$Y=2.123+53.729e^{-.2159X}$	
NH_4^{+}	10	E	$Y=-.149+.5125e^{-.2159X}$	Natural sources.
NO_3^{-}	11,1	E	$Y=.3004+.0977e^{.00051X}$	Natural sources.
	11,2	B *	$Y=1572.9-1570.6e^{.0000106X}$	High concentration source, urban.

*Horizontal component only.

Table IV. The stations used to compute the quantitative models, listed by the element or compound examined. All 33 stations were used for quantitative models of K^+ and NH_4^+. There is no quantitative model for SO_4^{--}.

Ca^{++}	Na^+	Cl^-	NO_3^-
Quantitative Model 1*	Quantitative Model 1	Quantitative Model 1	Quantitative Model 1
Greenville, S. Carolina	Montgomery, Alabama	Caribou, Maine	Nantuckett, Massachusetts
Charleston, S. Carolina	Washington, D.C.	Nashville, Tennessee	Philadelphia, Pennsylvania
Caribou, Maine	Albany, New York	Montgomery, Alabama	Mongtomery, Alabama
Nantuckett, Massachusetts	Sterling, Virginia	Sault Ste. Marie, Michigan	Cape Hateras, N. Carolina
Washington, D.C.	Caribou, Maine	Grand Island, Nebraska	Tampa, Florida
Cape Hateras, N. Carolina	Cincinnati, Ohio	Glasgow, Montana	Charleston, S. Carolina
St. Cloud, Minnesota	Amarillo, Texas	Grand Junction, Colorado	Grand Junction, Colorado
Lake Charles, Louisiana	San Angelo, Texas	Pocatello, Idaho	Amarillo, Texas
Brownsville, Texas	Grand Island, Nebraska	Las Vegas, Nevada	Brownsville, Texas
San Angelo, Texas	Columbia, Missouri	Los Angeles, California	Lake Charles, Louisiana
Las Vegas, Nevada	St. Cloud, Minnesota	Amarillo, Texas	St. Louis, Missouri
	Chicago (OHare), Illinois		Nashville, Tennessee
Quantitative Model 2	Sault Ste. Marie, Mich.	Quantitative Model 2	Pocatello, Idaho
	Nashville, Tennessee		Tatoosh, Washington
Cincinnati, Ohio	Greenville, S. Carolina	Lake Charles, Louisiana	
Grand Junction, Colorado	Santa Maria, California	Columbia, Missouri	Quantitative Model 2
Grand Island, Nebraska	Grand Junction, Colorado	Sterling, Virginia	
Chicago (OHare), Illinois	Glasgow, Montana	Washington, D.C.	Caribou, Maine
Tampa, Florida	Pocatello, Idaho	Greenville, S. Carolina	Washington, D.C.
Albany, New York	Los Angeles, California	Chicago (OHare), Illinois	Cincinnati, Ohio
Sterling, Virginia	Las Vegas, Nevada	Philadelphia, Pennsylvania	Albany, New York
Montgomery, Alabama			Greenville, S. Carolina
Philadelphia, Pennsylvania	Quantitative Model 2	Quantitative Model 3	San Angelo, Texas
Nashville, Tennessee			Grand Island, Nebraska
	New Orleans, Louisiana	Albany, New York	Columbia, Missouri
Quantitative Model 3	Brownsville, Texas	Tampa, Florida	Chicago (OHare), Illinois
	Lake Charles, Louisiana	Chicago (Midway), Illinois	Saute Ste. Marie, Mich.
Columbia, Missouri	Tampa, Florida	Brownsville, Texas	St. Cloud, Minnesota
Chicago (Midway), Ill.	Chicago (Midway), Ill.	Charleston, S. Carolina	Los Angeles, California
	Charleston, S. Carolina		Chicago (Midway), Ill.
			Sterling, Virginia

* There is no general quantitative model 1, 2, or 3 (as in the general graphical models A, B&C, D and E). For each of the six elements and compounds examined here, two or three specific quantitative models were found to apply.

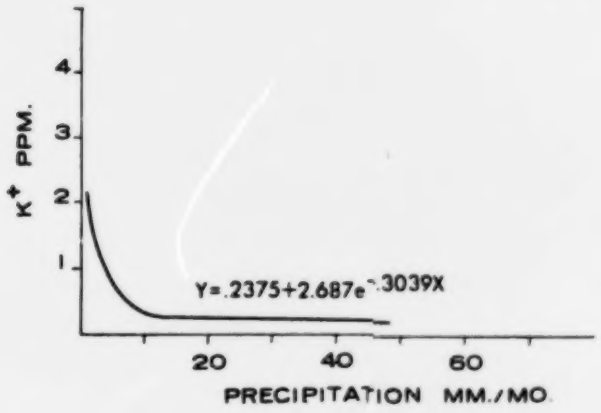


Figure 7. Quantitative model for K^+, showing pattern of graphical model A. Inputs are natural in origin.

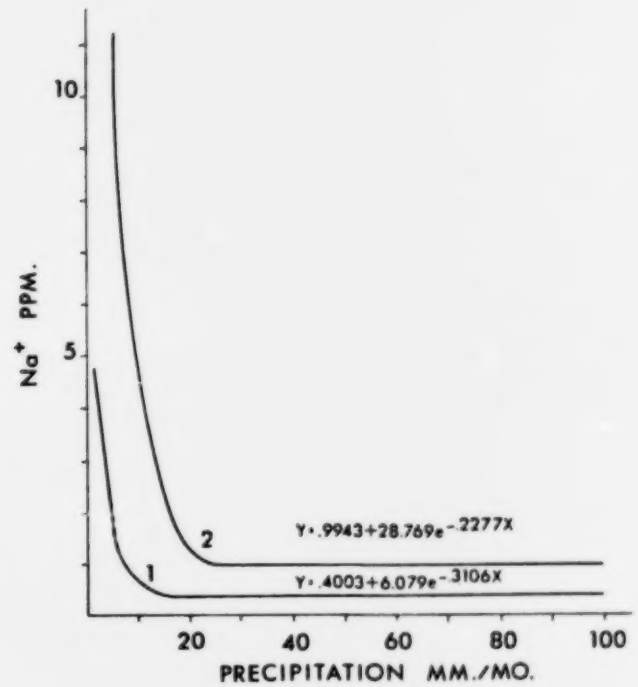


Figure 8. Quantitative models for Na^+, showing patterns of graphical models A and B. Inputs are natural and anthropogenic in origin. Curve 2 has higher natural input than curve 1, as indicated by a higher base level, but it is also richer in anthropogenic intrusions, as indicated by the upward-moving inflection point.

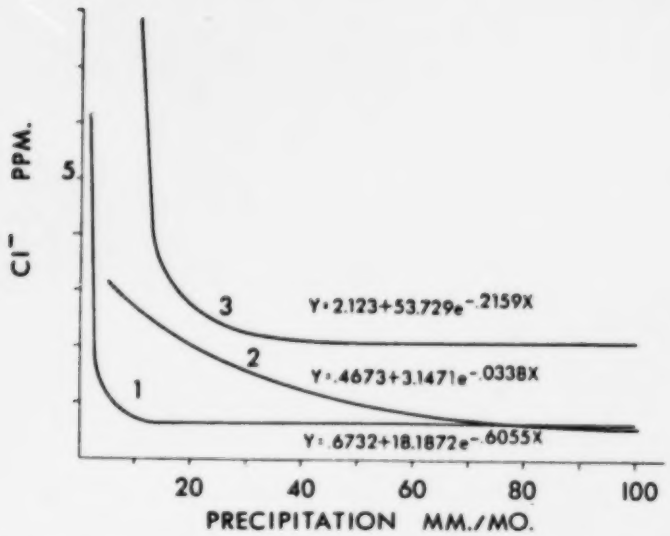


Figure 9. Quantitative models for Cl^-, showing patterns of graphical models A and B&C. Inputs are of natural and anthropogenic origin. Curves 2 and 3 show high concentration sources, natural and urban.

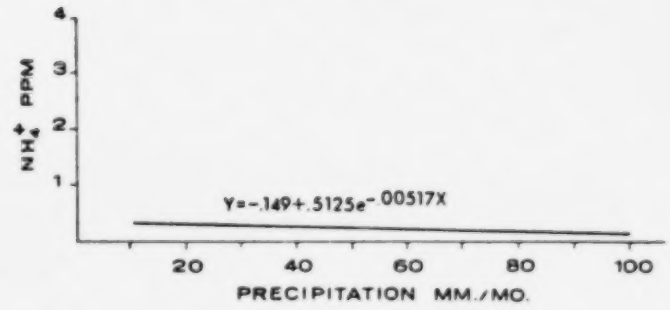


Figure 10. Quantitative models for NH_4^+, showing pattern of graphical model E. Inputs are of natural origin.

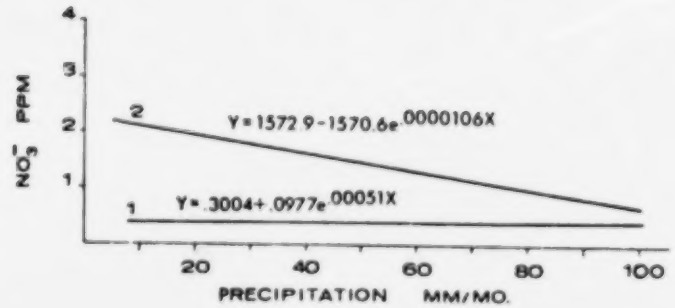


Figure 11. Quantitative models for NO_3^-, showing patterns of graphical models E and B (horizontal component only). Inputs are of natural and anthropogenic origin. Curve 2 shows high urban concentration sources.

Spatial Models

Contour maps were produced for each of the seven chemicals (Figures 12-32), to delineate air masses and sources of materials for rainout concentration (Figures 12-18), washout concentration (Figures 19-25; see page 30), and total wet fallout (Figures 26-32; see page 46). This method is helpful in delineating air masses by means of base level air mass concentration for the chemicals considered and in identifying sources. Comments on possible sources of components and discussion of patterns are given in the legends to the maps.

Spatial Models, Rainout

Table V gives the rainout concentrations at oceanic and continental stations for the seven chemicals sampled. The stations selected were either right on the coast or definitely in the interior of the U.S. These values are indicative of the actual concentration in the continental and marine air masses, since the factor of local intrusion (washout) has been eliminated. This concept of rainout could be extrapolated further with better sampling, i.e. sampling that differentiated between the many different marine and continental air flows.

In general, the rainout maps indicate that air masses are not normally influenced by the local intrusion of elements; the oceanic and continental air masses are quite well defined by Na^+ and Cl^-. This fact may become important for determining air mass origins.

Following are the rainout maps for the elements and compounds under consideration. Discussion of washout maps appears on page 30.

Table V. Average rainout concentration (ppm) of elements and compounds at continental and coastal stations.

ELEMENT/ COMPOUND	CONTINENTAL STATIONS	COASTAL STATIONS
Ca^{++}	.13	.25
K^+	.10	.10
Na^+	.10	1.27
Cl^-	.12	2.7
NH_4^+	.05	.05
NO_3^-	.10	.10
SO_{4--}	.40	.40

Figure 12. Ca^{++} Rainout Map.

The Ca^{++} rainout map shows the effects of marine and continental air masses. Coastal areas have a Ca^{++} concentration of 0.06 - 0.19 ppm, lower than the concentration of 0.19 - 0.4 ppm for the continental interior. It is interesting to note that the contours between levels 1 and 2 follow the major air flow patterns for the summer and spring seasons in the U.S. (BLAIR 1942).

Florida and southern Texas have higher values than other coastal areas, probably due to limestone bedrock. Similarly high values appear around urban industrial centers (Chicago, Illinois; Cincinnati, Ohio; and Columbia, Missouri) where the lime and gypsum manufacturing occur. Local intrusions may affect rainout concentrations; PETREMCHUK & PROZDIVA (1966) found that Cl^{-}, NO_3^{-} and SO_4^{--} increased with proximity to urban areas when he took precipitation samples within the cloud layer.

The high concentration of Ca^{++} around Pocatello, Idaho, may be due to an industrial point-source or to natural input of gypsum salt in that area. The significant correlation coefficient between Ca^{++} and SO_4^{--} concentrations (Table I) could indicate that $CaSO_4$ is the compound supplying this input of Ca^{++}.

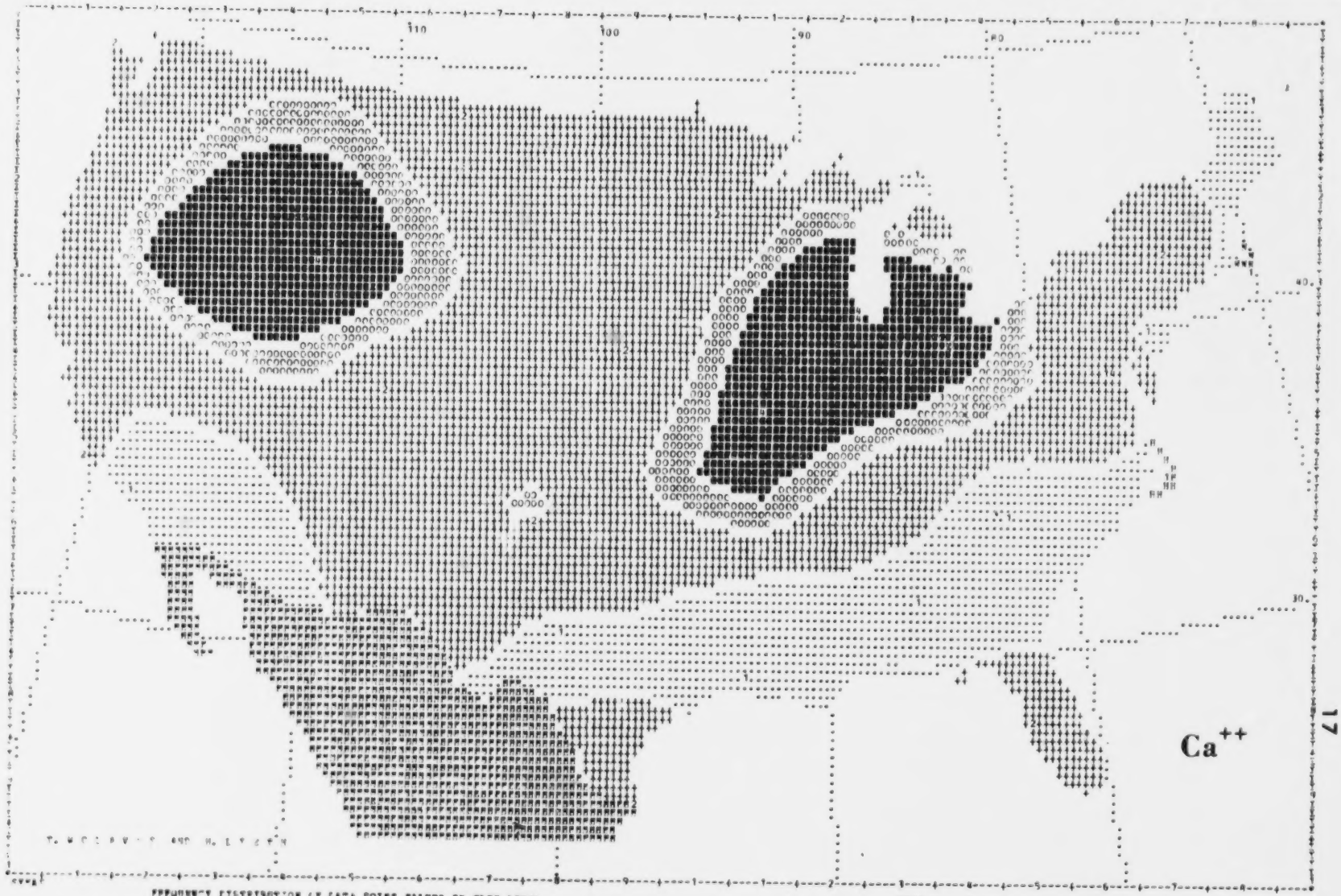


FIG. 12

Figure 13. K^+ Rainout Map.

Potassium has a low rainout input, ranging from .048 to .167. There appears to be a fairly uniform distribution with the exception of the high values along the west coast, around Grand Junction, Colorado, and around Chicago, Illinois. Oceanic aerosols may be causing the highs along the west coast, while local pollution and continental aerosols may cause the highs in Chicago and Grand Junction, respectively. The uniform inland distribution may be due to the general oceanic origins of K^+ in the air or to a predominantly terrestrial input of K^+ in continental regions which tends to be uniform and of levels equal to oceanic input.

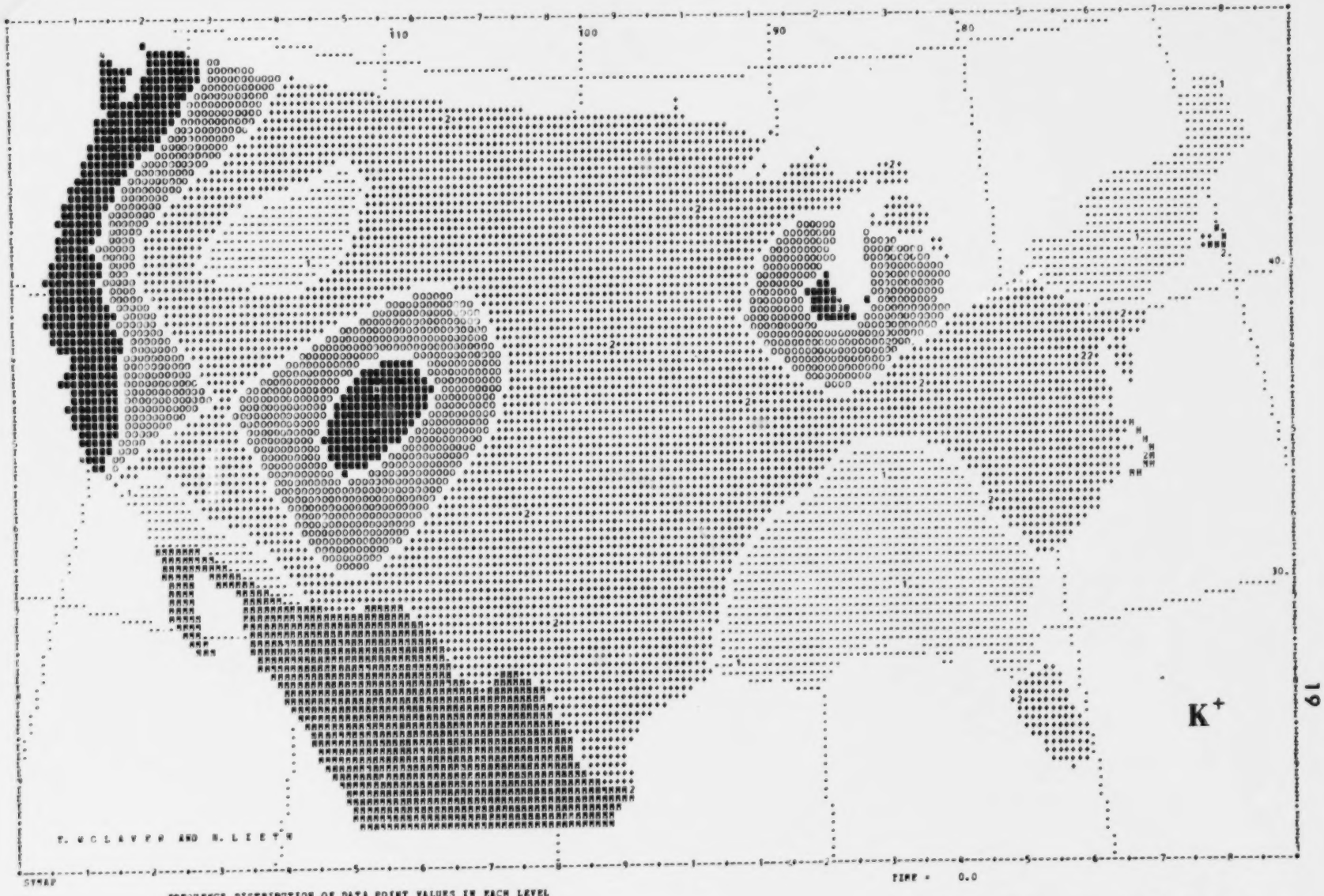

K+
19
SYMAP
FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL
LEVEL
SYMBOLS
FREQ.
MIN .048 .078 .108 .137 PPM.(K+)
MAX .078 .108 .137 .167

FIG. 13

Figure 14. Na^+ Rainout Map.

Sodium is a major constituent of seawater and the coastal areas, therefore, show high values for this element. A uniformly low value of 0.06 - 0.15 ppm is observed over the continental interior. The distribution of Na^+ rainout is a good indicator of the dominance of marine and continental air masses.

The sharply reduced Na^+ concentration away from the coast may be explained by the contention of BYERS *et al.*(1955) and JUNGE (1957), that convection near the coast transports NaCl vertically, lowering the concentration near the land surface and forming a uniform vertical distribution of NaCl particles.

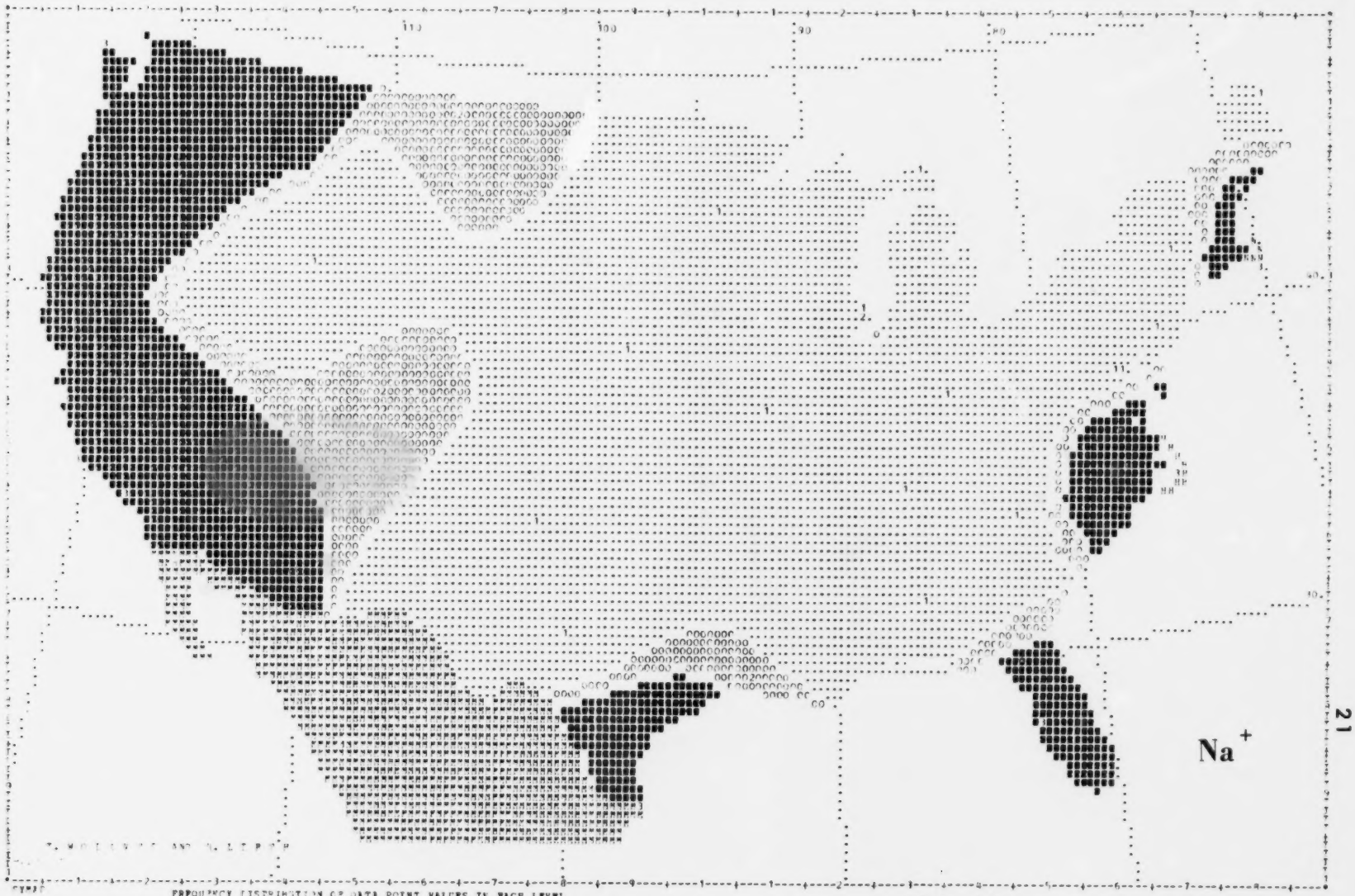

Na^+
FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL
LEVEL 1 2 3
SYMBOL
FREQ. 17 5 7
ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
(*MAXIMUM* INCLUDED IN HIGHEST LEVEL ONLY)
MIN. .067 .149 .199 PPM. (Na^+)
MAX. .149 .199 2.35
TIME = 0.0

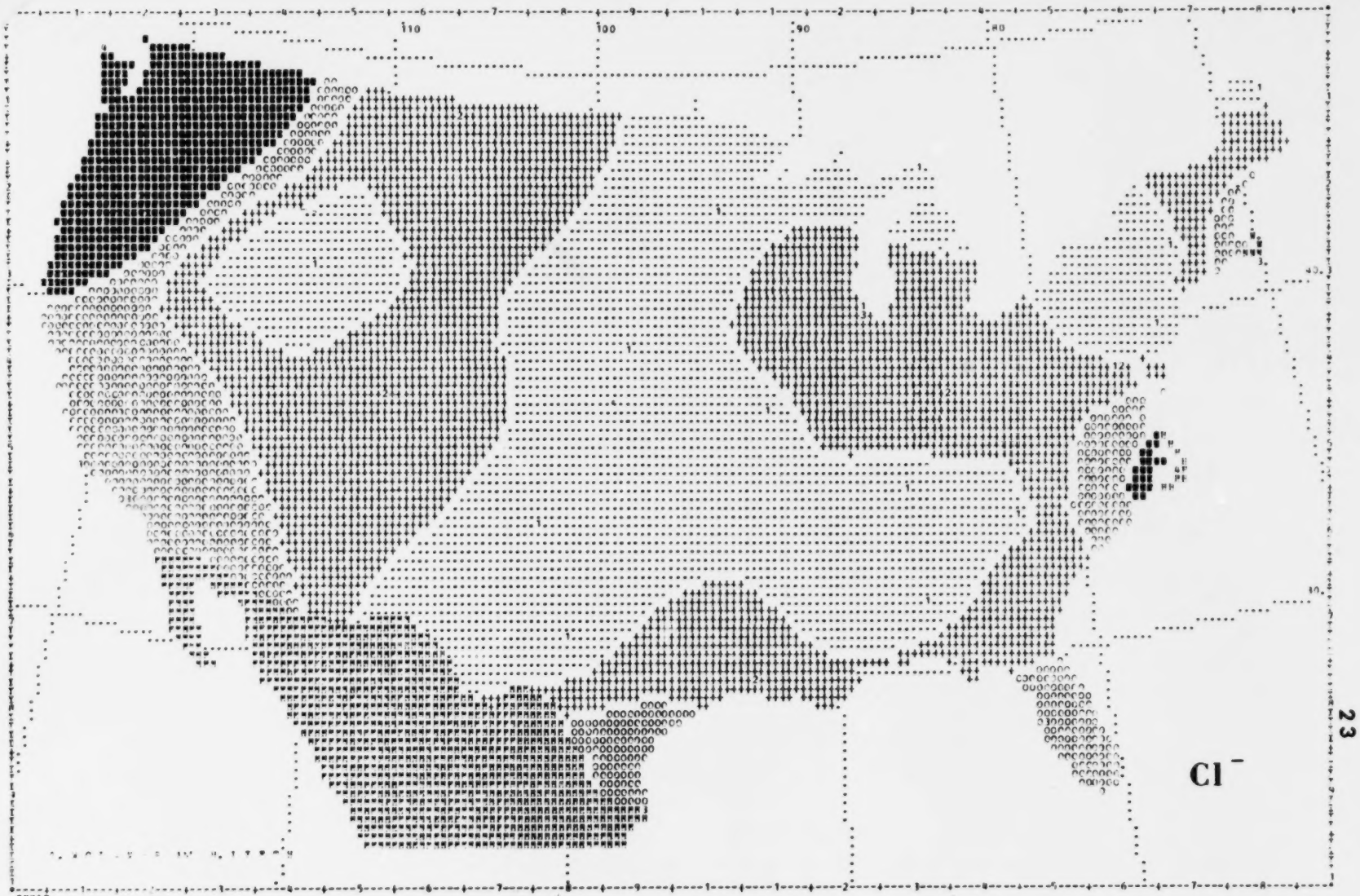
FIG. 14

Figure 15. Cl^- Rainout Map.

The chlorine rainout distribution follows the same general pattern as that of Na^+ which we would expect of this, the second major component of seawater. Along the coast one finds high concentrations around 0.5 - 2 ppm, while the interior averages around 0.1 ppm. In the northeastern U.S. one finds higher values than those of the rural interior. Quantitatively, Cl^- has about twice the concentration of Na^+ in many areas of the U.S. This would not occur if sea-salt aerosols were the only source of Cl^-. Since most of the stations are in urban areas, this suggests an additional, anthropogenic source of Cl^- in rainout.

LODGE et al. (1968) reduced the same data using other methods, and demonstrated that Cl^- concentration varies with the seasons, the higher values found in winter and fall and the lower found in spring and summer. This could be caused by the liberation of Cl^- during the heavy winter combustion of fossil fuel, probably the most significant anthropogenic source of Cl^-. This would explain the high concentration of Cl^- in the northeastern United States.

VALACH (1967), on the other hand, has considered the origin of the gaseous forms to be natural atmospheric Cl^-.



FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL

LEVEL	1	2	3	4
SYMBOL	.	+	C	#
FREQ.	15	6	6	7

ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
('MAXIMUM' INCLUDED IN HIGHEST LEVEL ONLY)

MIN.	.05	.202	.401	.964	PPM. (Cl^-)
MAX.	.202	.401	.964	3.75	

C MOTAYNE, T. AND LEWIN, H.: USA , B.L.,Cl- (PPM)

C DATA SOURCE: ARCO, SATEL RESEARCH, I. TABOR AND S. MCCORMICK

C MEXICO ESSIGNATED BY M, WASHINGTON BY W, PPT CAPE HALATAS BY P.

FIG. 15

Figure 16. NH_4^+ Rainout Map.

The map of ammonium rainout indicates that, as for K^+, there are no important continental sources. A uniform value of 0.03 - 0.09 ppm is observed.

JUNGE (1963) indicates that NH_4^+ appears to have a high concentration inland and tapers off toward coastal areas, with ratios for the air masses being

tropical : polar : arctic :: 1.00 : 0.74 : 0.49.

This trend may be misleading due to JUNGE's method of analyzing concentration data, which is probably biased toward washout material of local origin. It is possibly the effect of his not excluding the dry fallout in his collections.

The rainout determinations following the method used for this paper indicate a fairly uniform NH_4^+ concentration throughout the marine and continental air masses, implying that sources are either oceanic with little rainout, or continentally uniform. Ammonium in rainwater has been attributed to continental sources such as fertilizers, soil exhaustion and industry.

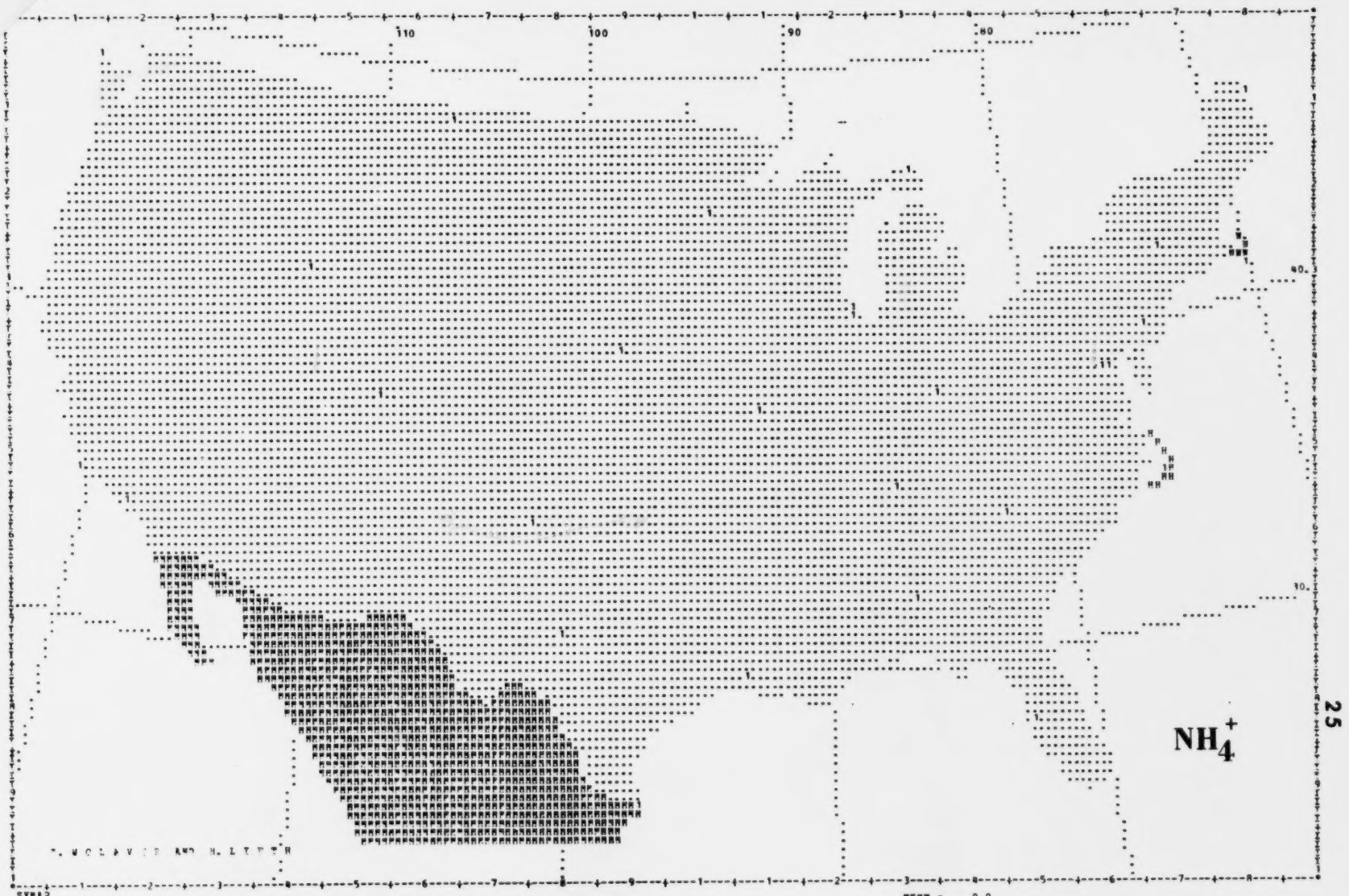

110
100
90
80
40.
30.
25
NH_4^+
FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL
LEVEL 1
SYMBOLS 1
FREQ. 29
ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
('MAXIMUM' INCLUDED IN HIGHEST LEVEL ONLY)
MIN. .02 PPM. (NH_4^+)
MAX. .09
TIME = 0.0
C WOLAVER, T. AND LISTER, H.: USA , B.L.,NH_4^+(PPM)
C DATA SOURCE: APCO, NATL NETWORK, E. TABOR AND P. MCCORMICK
C MEXICO DESIGNATED BY M, NANTUCKET BY N, AND CAPE HATTERAS BY H.

FIG. 16

Figure 17. NO_3^- Rainout Map.

Nitrate, another compound of supposed anthropogenic source, has a very uniform rainout concentration in both coastal and continental areas. The low value of 0.03 - 0.16 ppm can be attributed to oceanic sources, since little variation in NO_3^- rainout concentration occurs over the continent. Also, there is a very high percentage of NO_3^- found in washout (Table VI) and very little in rainout. Two exceptions to the uniform concentration are the Los Angeles Basin and the Chicago area, both noted for their high concentration of pollutants, including nitrogen oxides. A peculiar phenomenon is that the northeastern industrial centers do not show the same high values of NO_3^- in rainout.

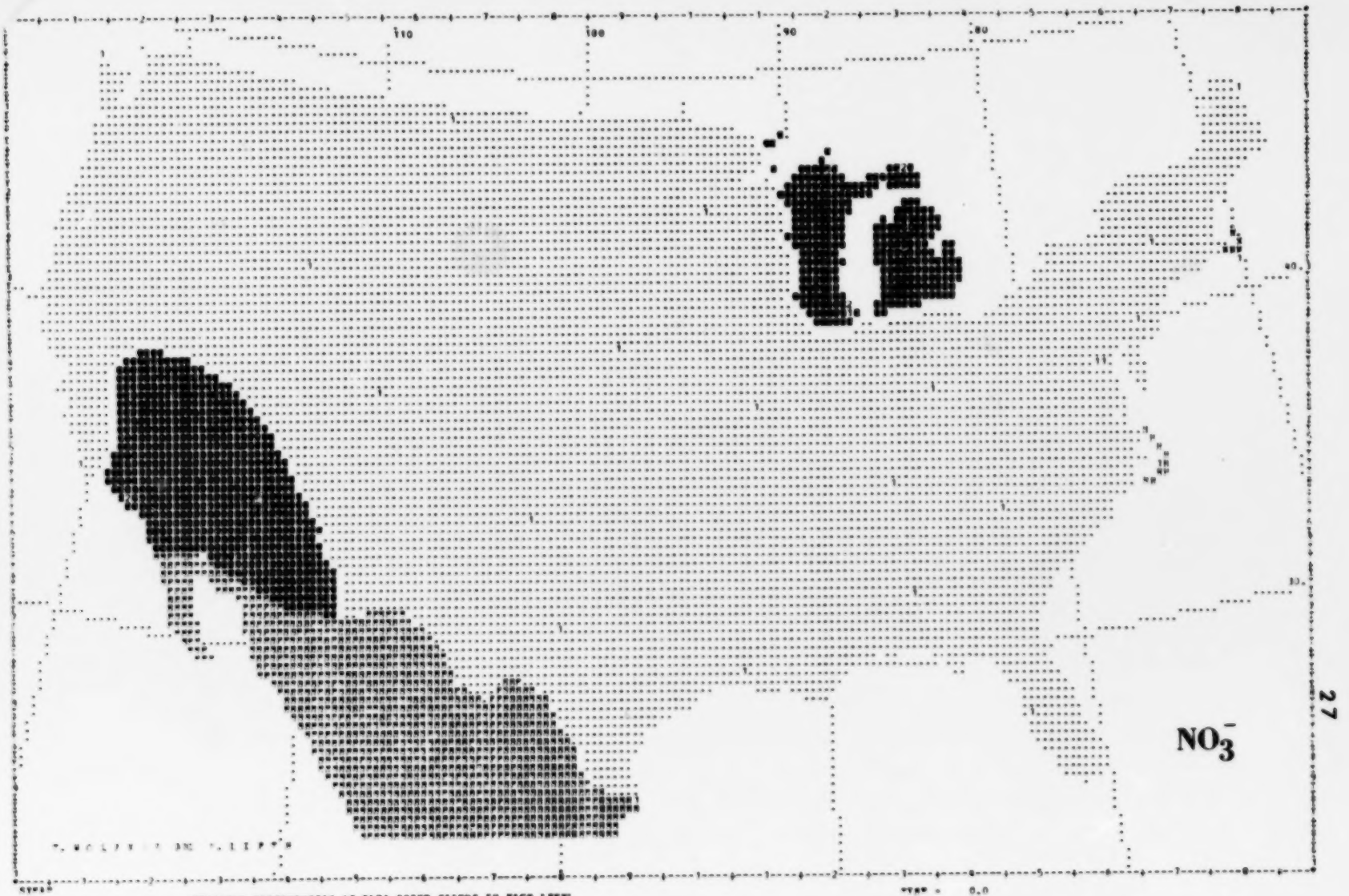


FIG. 17

Figure 18. SO_4^{--} Rainout Map.

Sulfate rainout concentrations indicate that its major sources are local anthropogenic origins. There is no real difference between continental and marine air masses except in the urban areas, implying that in rural areas sulfate can be attributed to an oceanic source with little rainout, or to a uniform inland source. Sulfate in rainout varied to a great extent depending on the urban center sampled, with the extreme values occurring in the northeastern industrial areas.

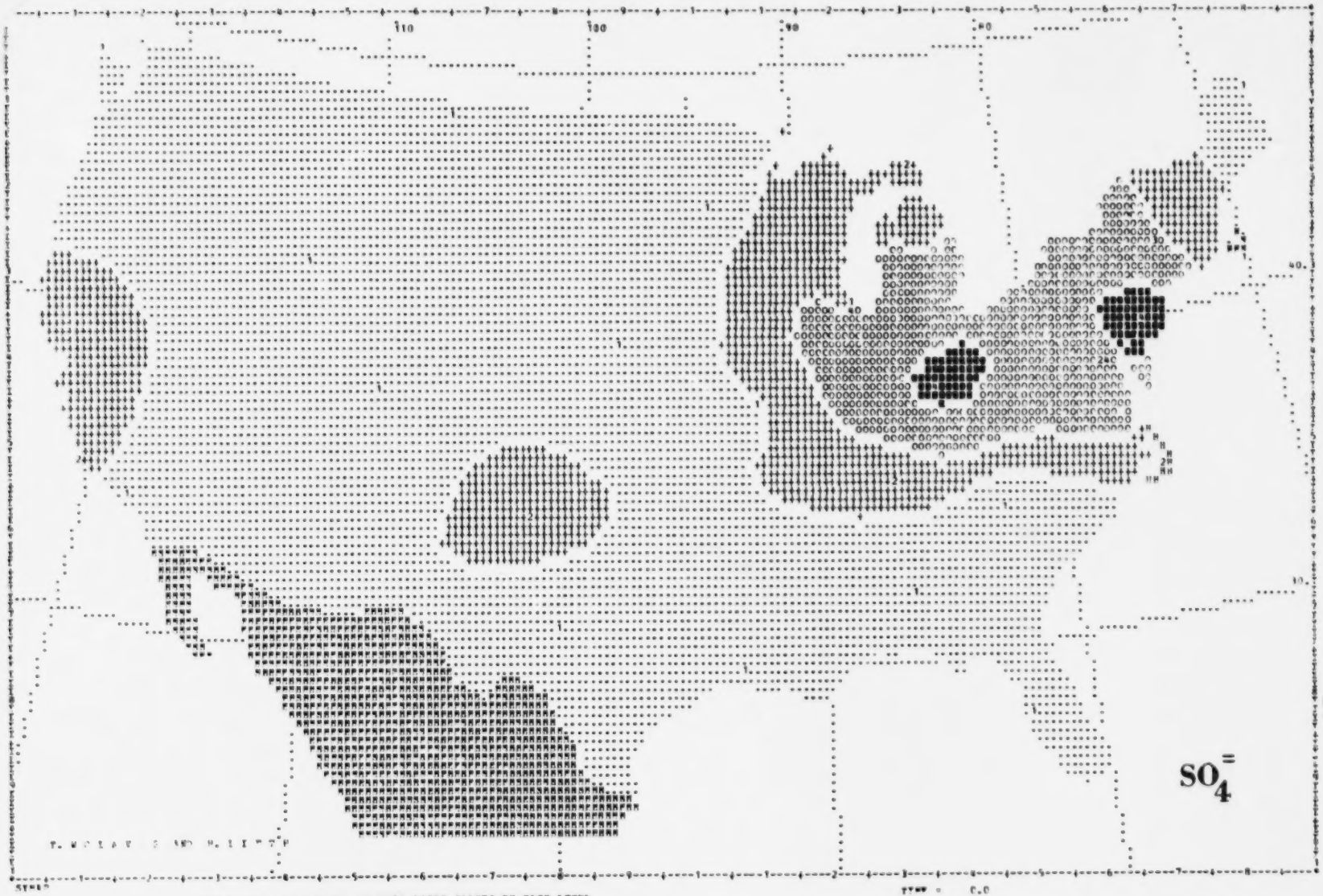


FIG. 18

MIN.	.03	.865	1.61	3.14	PPM.($SO_4^=$)
MAX.	.865	1.61	3.14	4.67	

Spatial Models, Washout

In most cases, washout accounts for most of the chemical input for the yearly total. Table VI gives an idea of the amount of material (%) that is input via washout for 29 of the 33 stations. These percentages indicate that NO_3^- is almost solely of local intrustion, with usually greater than 90% of this compound found in washout. The six other chemicals have percentages greater than 50% and show little relation between physical location and washout. There is some indication that an area of high continental aerosol input will show a high percentage of chemical washout, and an area of little or no continental aerosol input will show a lower percentage of chemical washout. These two area types are exemplified by Grand Junction, Colorado, and St. Cloud, Minnesota, respectively.

The following contour maps of washout (Figures 19-25) resemble the excess ionic maps of JUNGE & WERBY (1958), but they seem to circumscribe the source areas more precisely. We conclude from the washout maps that the process of washout accounts for a major portion of the material that is collected from rainwater. Both the natural elements Ca^{++}, K^+, Na^+, and Cl^-, and the compounds of supposed human origin NH_4^+, NO_3^-, and SO_4^{--}, have natural and anthropogenic sources. These sources include sea-salt and continental aerosols, industrial pollutants, and combustion of fossil fuels.

Discussion of total wet fallout maps is on page 46, following the washout maps.

Table VI. Percentage of material imputed through washout.

STATION*	Ca^{++}	K^{+}	Na^{+}	Cl^{-}	NH_4^{+}	NO_3^{-}	SO_4^{--}
1 Caribou, Me.	63	24	36	41	79	93	78
2 Nantuckett, Mass.	82	55	82	82	42	84	84
3 Albany, N.Y.	77	88	80	86	76	90	73
4 Philadelphia, Pa.	74	54	80	94	65	84	26
5 Washington, D.C.	25	23	58	54	54	95	33
6 Cincinnati, Ohio	75	26	74	74	75	96	52
7 Sterling, Va.	76	48	74	63	78	97	51
8 Montgomery, Ala.	79	46	80	71	67	88	81
9 Tampa, Fla.	83	50	75	75	68	87	92
10 Greenville, S.C.	80	58	72	69	74	91	73
11 Charleston, S.C.	66	50	79	70	55	89	84
12 Nashville, Tenn.	70	31	49	48	57	87	45
13 Chicago (Midway),Ill.	79	68	82	84	81	93	69
14 Chic. (O'Hare), Ill.	84	59	82	82	85	76	94
15 Sault Ste. Marie,Mich	84	58	68	87	79	49	64
16 St. Cloud, Minn.	74	25	25	45	88	97	68
17 Columbia, Mo.	85	63	55	62	38	92	72
18 Gr. Island, Neb.	76	54	68	49	75	96	80
19 Lake Charles, La.	74	37	63	74	71	97	62
20 Amarillo, Tex.	82	64	80	73	35	89	56
21 Brownsville, Tex.	72	43	51	68	25	90	-
22 San Angelo, Tex.	96	77	97	97	40	89	83
23 Gr. Junction, Colo.	97	88	81	81	80	97	96
24 Pocatello, Idaho	79	83	90	87	83	70	98
25 Glasgow, Mont.	73	73	86	77	87	96	99
26 Los Angeles, Cal.	88	61	61	82	97	89	57
27 Santa Maria, Cal.	76	83	82	84	-	93	-
28 Tatoosh, Wash.	78	89	90	87	75	71	81
29 Cape Hatteras, N.C.	81	64	66	73	30	85	74

* The remaining stations from which data were taken for this paper are listed below:

30 New Orleans, La.
31 Santa Catalina, Cal.
32 St. Louis, Mo.
33 Las Vegas, Nev.

These stations did not have complete data and were used in total wet fallout studies only. Where data was missing, extrapolations were made from expected precipitation and elemental concentrations.

- - - - - - - -

The following two stations were used in total wet fallout studies for specific elements and compounds, as listed:

34 Research Triangle Park, N.C. (Ca^{++}, K^{+}, NH_4^{+}, NO_3^{-})(WELLS et al. 1972)
35 Coweeta Exp. Sta., N.C. (Na^{+}, K^{+}, Ca^{++}) (BEST 1971)

Figure 19. Ca^{++} Washout Map.

The Ca^{++} washout contour map clearly shows inputs due to surface salts and industrial sources. High values throughout the Southwest can be attributed to soil salts $CaCl_2$, $CaSO_4$, and $CaCO_3$. Correlation coefficients (Table I) for Ca^{++} and Cl^-, and for Ca^{++} and SO_4^{--}, show high associations for this area. Unfortunately, CO_3^{--} concentrations were not determined in the rainwater samples, and no correlation coefficient could be derived for Ca^{++} and CO_3^-.

High values around Illinois, Ohio, and New York City are du to industrial sources since a great deal of lime and gypsum manufacturing takes place in those areas. Through the Florida panhandle and southern California, Ca^{++} is locally intruded due to limestone bedrock.

In general, Ca^{++} has high washout concentrations in many areas having continental aerosols of $CaCl_2$, $CaSO_4$, and $CaCO_3$, and in those areas having point-sources of these compounds due to industrial processing. A noticeably lower value is found where no local intrusions occur.

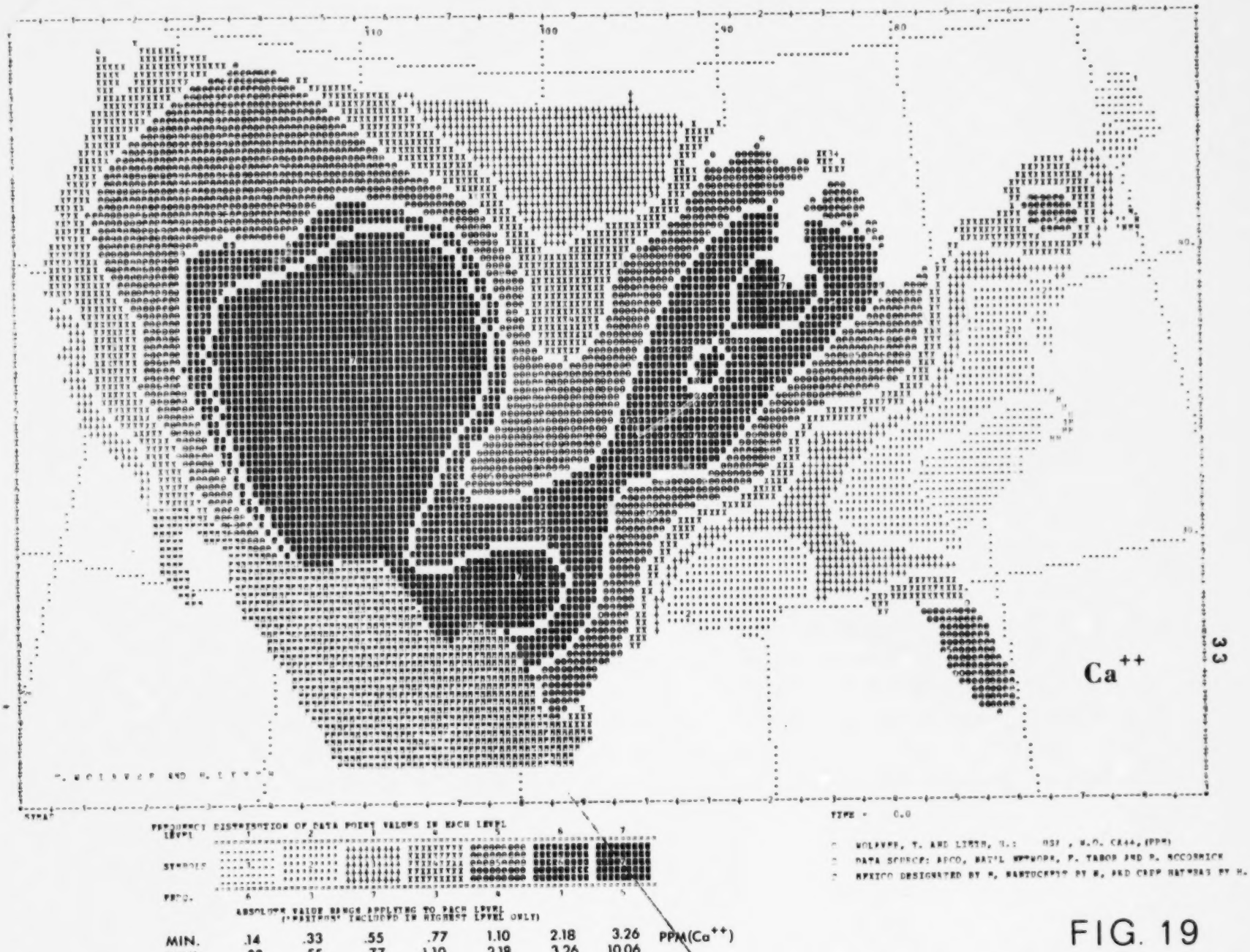

Ca++
33
TIME = 0.0
MIN. .14 .33 .55 .77 1.10 2.18 3.26 PPM(Ca++)
MAX. .33 .55 .77 1.10 2.18 3.26 10.06

FIG. 19

Figure 20. K^+ Washout Map.

The K^+ washout distribution is similar to that of the other natural elements, testifying to similar sources; particularly, continental aerosol and industrial point sources. High values throughout the Southwest and Northwest are due to continental aerosols bearing KCl from the arid areas; high correlation coefficients for K^+ and Cl^- (Table I) throughout this area suggest KCl as the most likely source. The absolute values of K^+ are not large since high concentration sources do not exist. Slight increases around urban centers such as Chicago and New York City may be due to combustion of fossil fuels releasing K^+, or to chemical manufacturing.

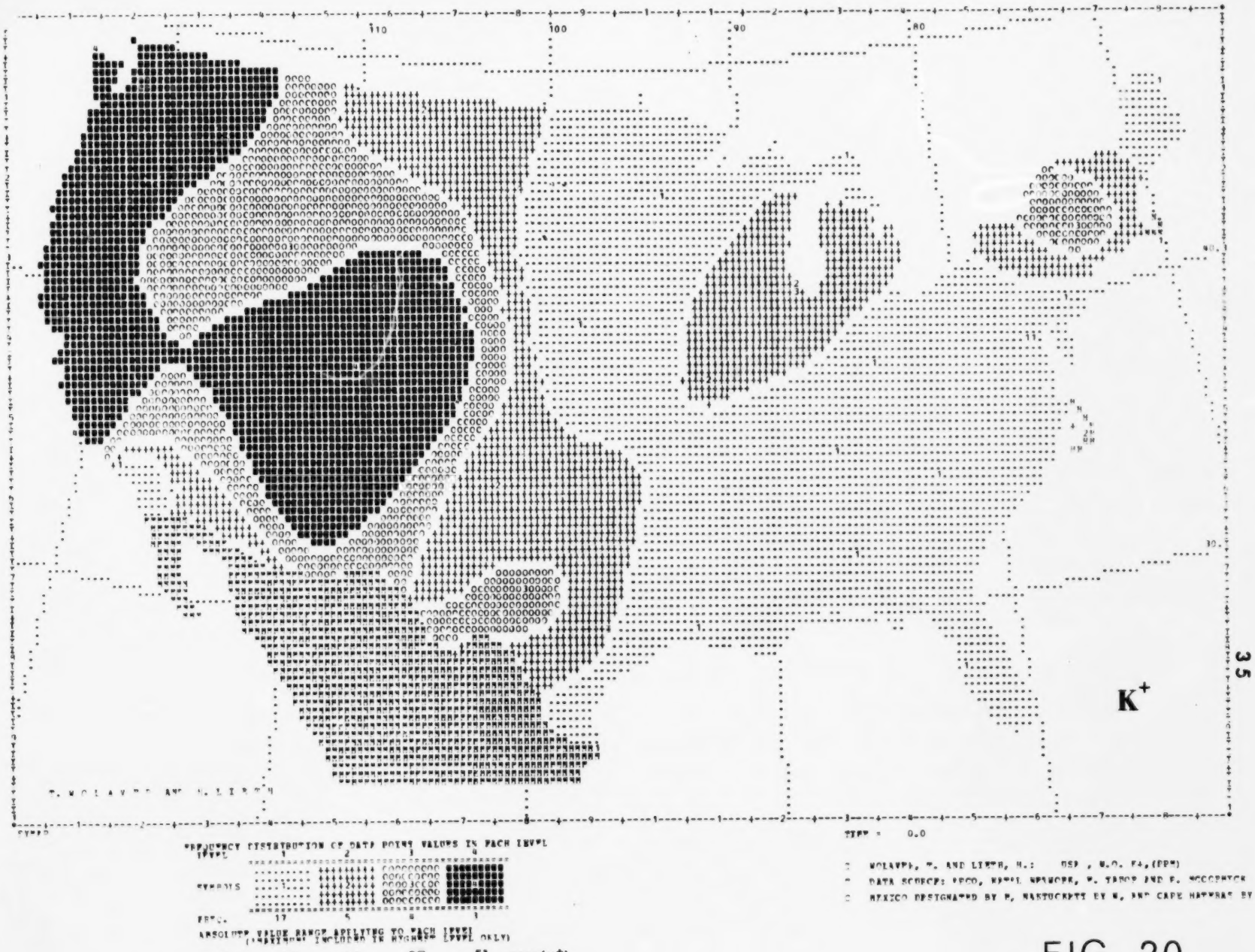

110
100
90
80
K+
35
STEP = 0.0
FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL
LEVEL 1 2 3 4
SYMBOLS
FREQ. 17 8 5 1
ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
MIN. .02 .14 .27 .51 PPM(K+)
MAX. .14 .27 .51 1.15

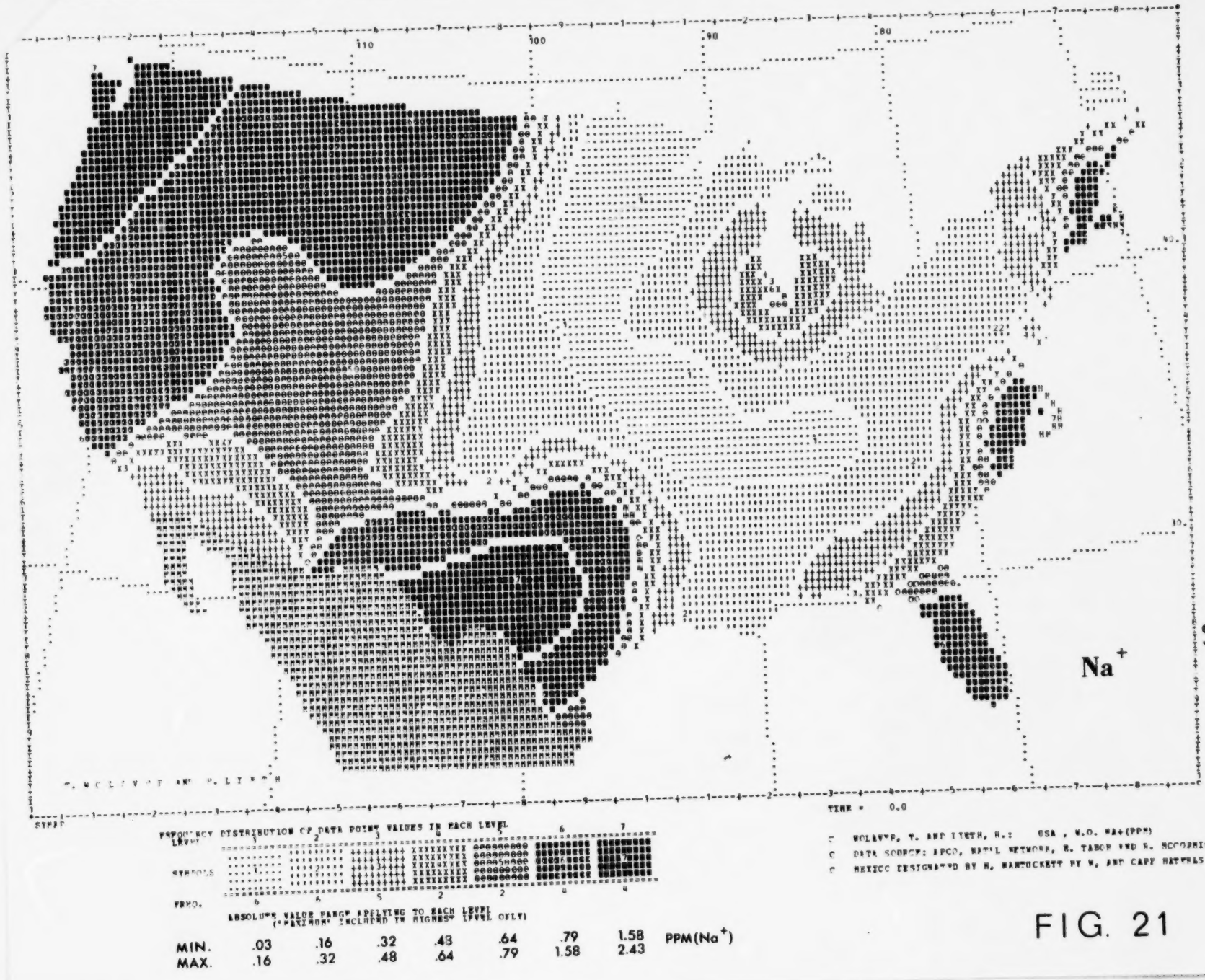
FIG. 20

Figure 21. Na^+ Washout Map.

The Na^+ washout distribution shows this element has many natural sources. High washout concentrations along coastal areas are caused by sea-salt aerosols; the Southwest shows the importance of continental aerosols. The high values in southern Texas show clearly the intrusion due to salt flats near the coast.

Correlation coefficients for Na^+ and Cl^- (Table I) in both urban and rural areas demonstrate that NaCl is probably the compound responsible for Na^+ input.

Sodium is a natural element and few anthropogenic sources exist. Very slight increases throughout the industrial Northeast may be attributable to combustion of fossil fuels, but little is known on this subject.


Na+
TIME = 0.0
FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL
LEVEL
SYMBOLS
FREQ.
ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
("MAXIMUM" INCLUDED IN HIGHEST LEVEL ONLY)
MIN. .03 .16 .32 .48 .64 .79 1.58
MAX. .16 .32 .48 .64 .79 1.58 2.43
PPM(Na+)
C WOLEVP, W. AND TYETH, H.: USA , W.O. NA+(PPM)
C DATA SOURCE: EPCO, NATL NETWORK, H. TABOR AND N. SCCORRICK
C MEXICO DESIGNATED BY N, MANCHUCKETT BY W, AND CAPE HATTRAS BY H.

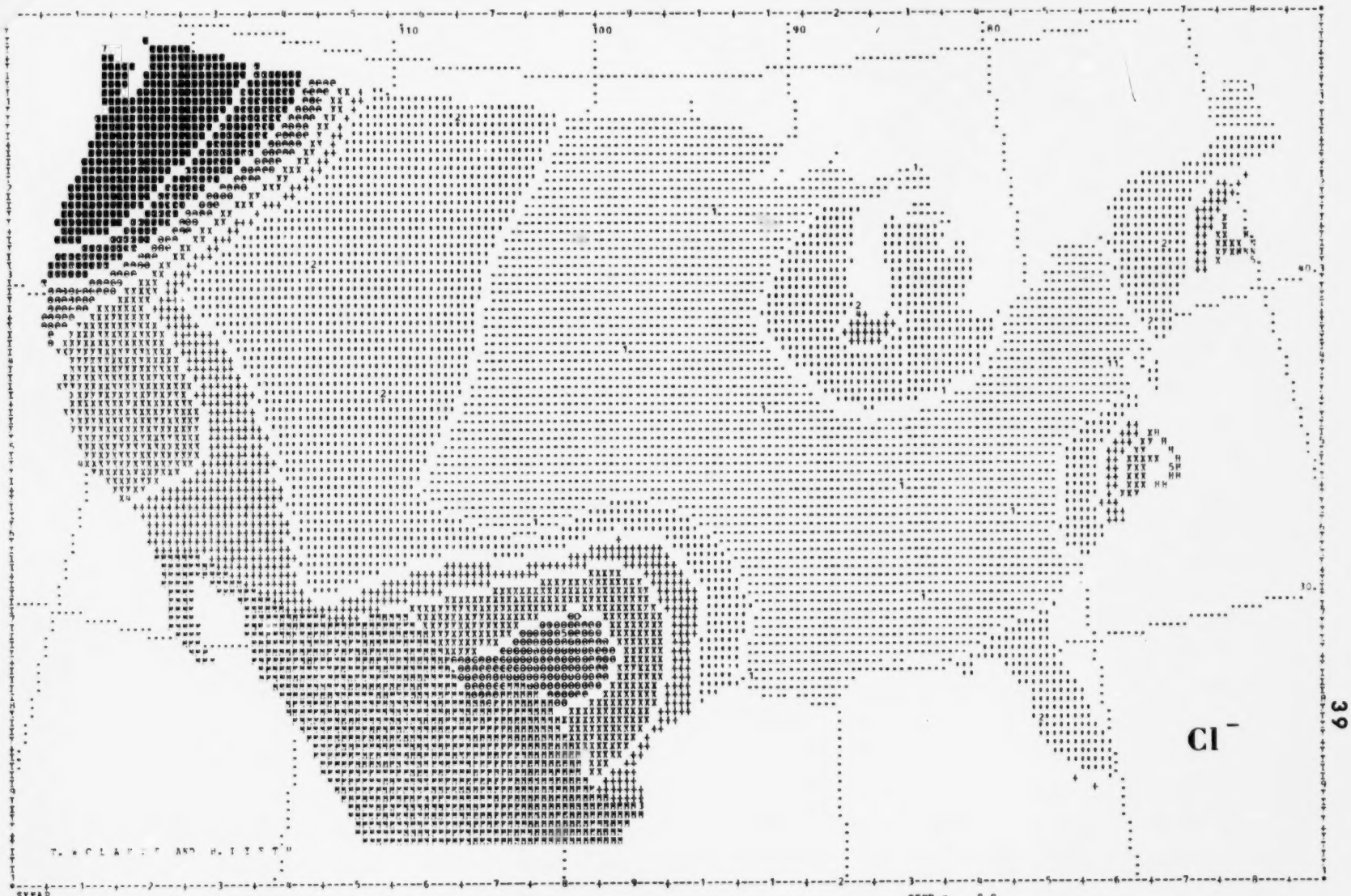
37

FIG. 21

Figure 22. Cl^- Washout Map.

The chlorine washout map shows the strong influence of marine air masses along the coast. High values through southern Texas show the effect of terrestrial NaCl salt flats in that area. In addition, the generally high values of Cl^- washout through the western arid areas that merge with the Pacific marine influence show continental aerosols laden with $CaCl_2$, KCl, and NaCl as an important source. A cursory inspection shows that the incidence of Ca^{++}, K^+, and Na^+ concentrations agrees rather well with that of Cl^- washout throughout the Southwest, as would be expected if these elements are assumed to derive from $CaCl_2$, KCl, and NaCl.

Chlorine is considered a natural element but large intrusions of anthropogenic Cl^- are observed in Illinois and Ohio, and throughout the Northeast. This industrial intrusion is in agreement with the findings of GEORGII & WEBER (1960) in Germany, and LODGE *et al.* (1968) in the U.S. Industrial sources and commercial combustion of fossil fuels seem to be responsible for this input.



FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL

LEVEL	1	2	3	4	5	6	7
SYMBOLS	.	+	X	H	S	M	@
FREQ.	11	8	1	3	1	0	1

ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
(*MAXIMUM* INCLUDED IN HIGHEST LEVEL ONLY)

	1	2	3	4	5	6	7	
MIN.	.11	.78	1.55	2.32	3.81	7.49	14.95	PPM(Cl^-)
MAX.	.78	1.55	2.32	3.81	7.49	14.95	24.16	

*TYPE = C.0

C WOLAVER, T. AND LYSH, H.: USA , W.O. CL-(PPM)
C DATA SOURCE: APCO, NATL NETWORK, Z. TABOR AND P. MCCORMICK
C MEXICO DESIGNATED BY M, NANTUCKETT BY N, AND CAPE HATTERAS BY H.

FIG. 22

Figure 23. NH_4^+ Washout Map.

Ammonium is a compound whose sources are hard to pin down, as was also found by JUNGE & WERBY (1958). The NH_4^+ washout map shows, in a general way, the same trends as those found by JUNGE & WERBY (1958). The higher values of ammonium through the northeastern states and the Los Angeles Basin can be explained by either industrial input or, speculatively, by liquid NH_4^+ fertilizers which are used extensively throughout southern California where there is a high evaporation rate. Low values are found throughout the Northwest and Southeast, in agreement with JUNGE (1958), although the delineation of the yellow and red laterite soils in the Southeast which he found does not appear on our map.

Other suggested ammonium sources are lightening and photochemical processes, ocean surface slicks, soil dusts, and bacterial action in soils. ANGSTRÖM & HÖGBERG (1952) have shown that lightening is not a significant source of NH_4^+. Photochemical processes have been discussed (ANGSTRÖM & HÖGBERG 1952, VIRTANEN 1952) but the data is too inconsistent for this to be regarded as a major source. GAMBELL & FISHER (1964) found that NO_3^- and NH_4^+ concentrations parallel that of SO_4^{--}, which is basically derived from SO_2. Similarly, the gaseous form of nitrogen may be a source of nitrogen compounds. All of these processes may be at work in the United States, but it is impossible to pinpoint any particular source using our washout map of NH_4^+.

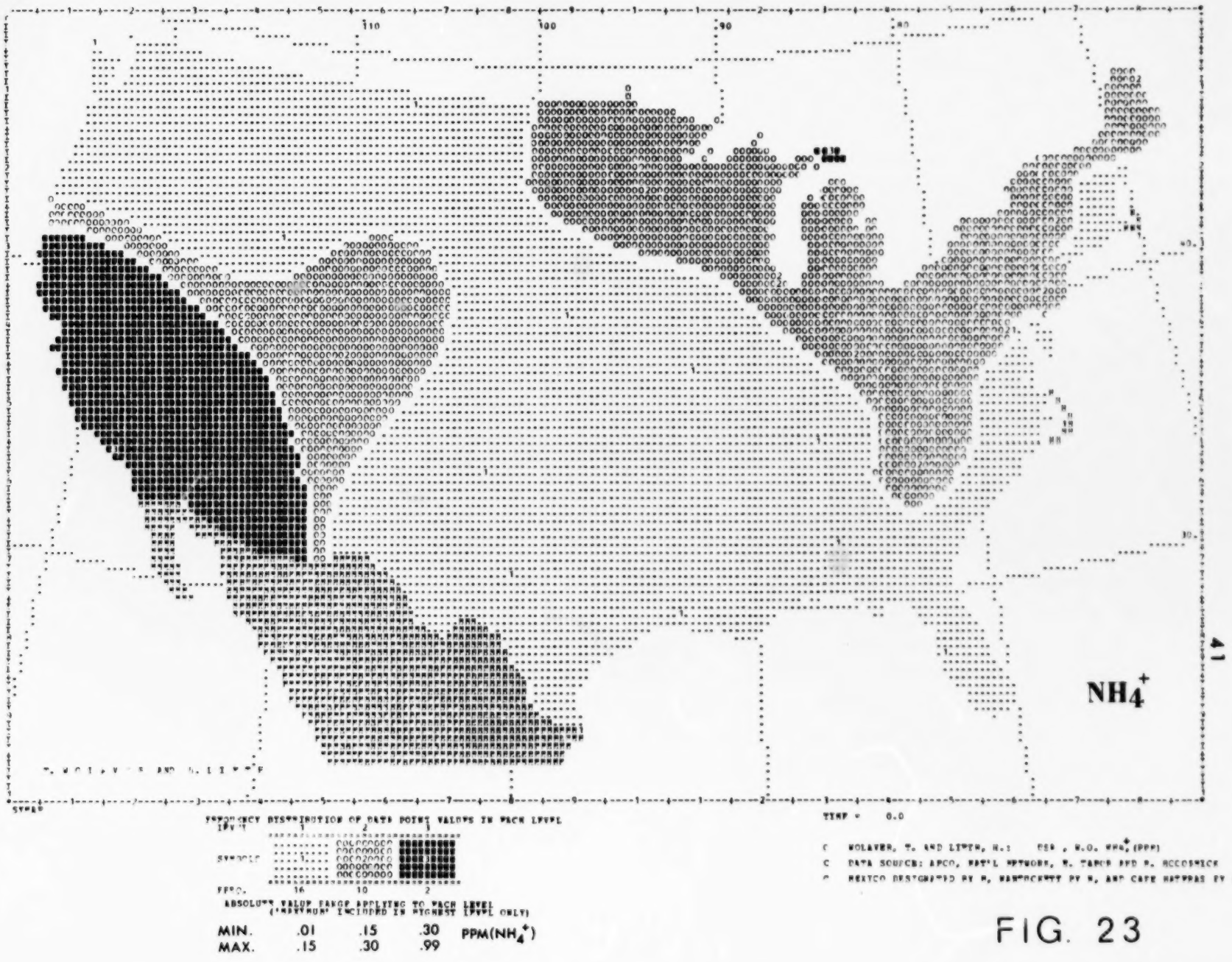
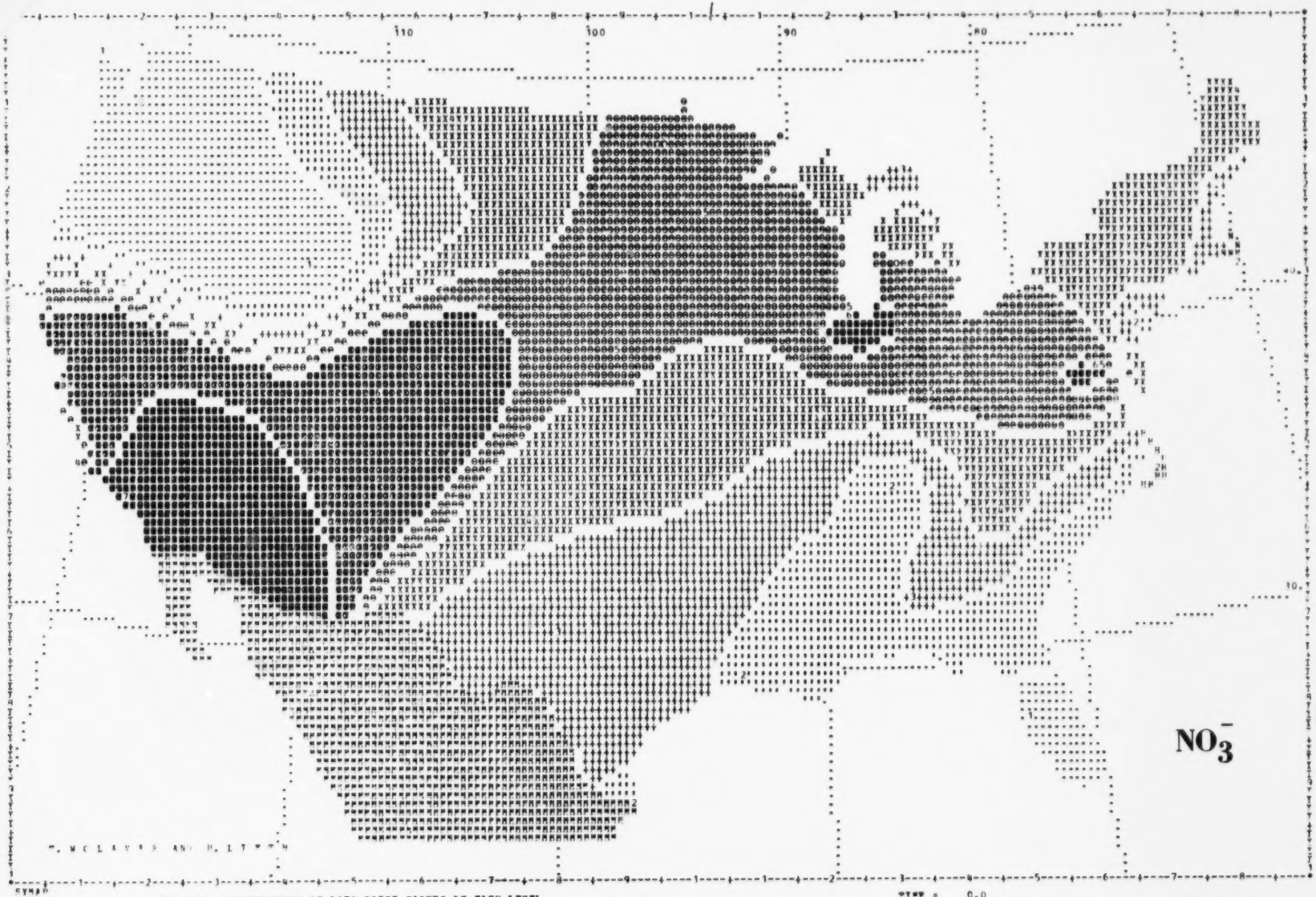

110
100
90
80
70
60
50
40
30
NH_4^+
SYMBOL
FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL
SYMBOL
FREQ.
16
10
2
ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
('MAXIMUM' INCLUDED IN HIGHEST LEVEL ONLY)
MIN. .01 .15 .30
MAX. .15 .30 .99
PPM(NH_4^+)
TIME = 0.0
C MOLAVER, T. AND LIPEN, H.: CSR , N.O. NH_4^+(PPP)
C DATA SOURCE: APCO, NATL NETWORK, N. TAPCB AND N. ACCOSWICK
C NEXTCO DESIGNATED BY N, HAMPOCKETT BY N, AND CAPE HATTRAS BY N.

FIG. 23

Figure 24. NO_3^- Washout Map.

Nitrate washout, in a very general way, follows the same distribution as NH_4^+, in agreement with the findings of JUNGE & WERBY (1958). Nitrate may therefore have some of the same sources as does NH_4^+. The high values in southern California correlate well with NH_4^+ values, probably due to fertilizer input and nitrogen oxide pollution from the Los Angeles Basin. Low values throughout the Southeast and Northwest may be caused by soil patterns, since soil pH is an important factor in the soil's release of ammonium, and possibly of NO_3^- also. ANDERSON (1915) showed that in the rural areas of the United States, the maximum amount of soil nitrate was found in spring and/or summer, indicating that biological activity in the soil is one source of nitrate. Higher values of nitrate washout occur throughout the northeastern industrial area, probably indicating the importance of the absorption of NO_2 gas of anthropogenic origin into rainwater (GEORGII 1963). It would appear that the most significant sources of NO_3^- in washout are anthropogenic.


110
100
90
80
43
NO_3^-
C MOLAVPE, T. AND LIESH, H.: USA , W.O. NO_3^-(PPP)
C DATA SOURCE: APCO, METRO METHODS, R. MANOR AND F. MCCORMICK
C MEXICO DESIGNATED BY M, NANTUCKETT BY N, AND CAPE HATARAS BY P.

FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL

LEVEL	1	2	3	4	5	6	7
SYMBOLS	.	:	+	X	@	#	
FREQ.	1	7	3	7	5	1	1

ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
(*MAXIMUM* INCLUDED IN HIGHEST LEVEL ONLY)

MIN.	.09	.25	.44	.64	.84	1.04	2.03	PPM(NO_3^-)
MAX.	.25	.44	.64	.84	1.04	2.03	4.20	

TIME = 0.0

FIG. 24

Figure 25. SO_4^{--} Washout Map.

Sulfate has been considered a compound of solely anthropogenic origin. The sulfate washout map indicates that other sources may be of considerable importance. The high values of SO_4^{--} washout throughout the Southwest are due probably to continental aerosol washout in the form of $CaSO_4$. High correlation coefficients of Ca^{++} and SO_4^{--} (Table I) testify to this association. The Southwest and the Florida panhandle are areas of high input, possibly due to the transformation of $CaCO_3$ into $CaSO_4$ in the presence of SO_2 (JUNGE 1963).

The highs around the northeastern industrial areas may be explained by the well known process of SO_2 gas absorption by rainwater. The formation of SO_4^{--} in water droplets has been discussed by SCOTT & HOBBS (1967). The absorption of SO_2 into rainwater and the subsequent oxidation to SO_4^{--} reaches a limiting value in solution proportional to the amount of catalyst present, the partial pressure of SO_2, and the pH of the rainwater (ERIKSSON 1959).

The most interesting pattern of sulfate concentration is that shown along the coasts, quite possibly explained by the release of H_2S from intertidal flats (ERIKSSON 1959) and/or fogwater, which is noted for its high concentration of SO_4^{--} (HOUGHTON 1955). The sources for SO_4^{--} washout seem to be quite varied, encompassing both natural and anthropogenic origins.

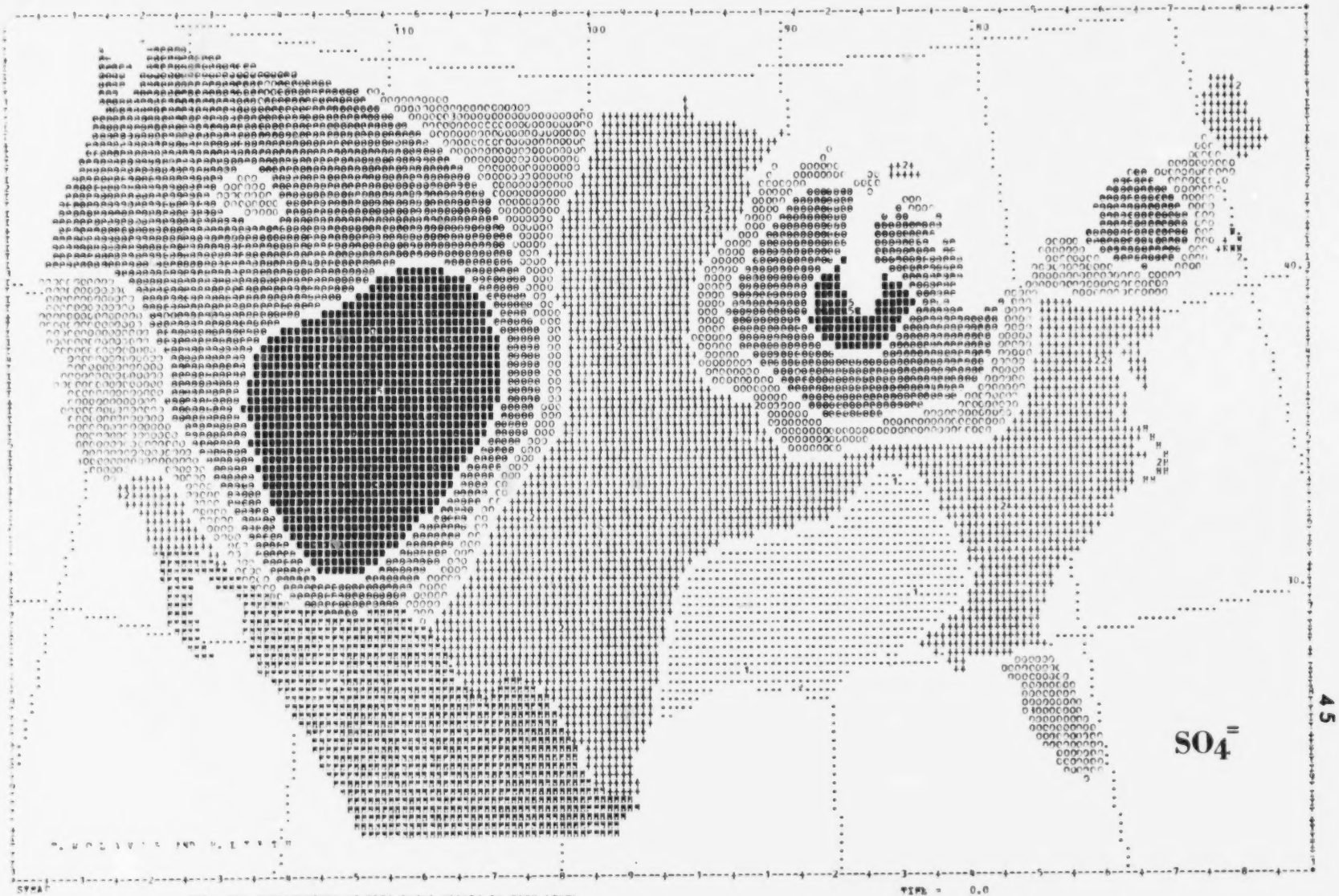

$SO_4^=$
45
FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL
LEVEL 1 2 3 4 5
SYMBOL
FREQ. 3 15 3 4 3
ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
(*MAXIMUM* INCLUDED IN HIGHEST LEVEL ONLY)
MIN. .56 1.17 2.25 3.33 6.57
MAX. 1.17 2.25 3.33 6.57 13.73
PPM($SO_4^=$)
TIME = 0.0
C WOLAVER, T. AND LIGTH, H.: USA , W.O. $SO_4^=$ (PPM)
C DATA SOURCE: APCO, BAPL NETWORK, M. TABOR AND R. MCCORMICK
C MEXICO DESIGNATED BY M, KENTUCKY BY K, AND CAPE HATERAS BY H.

FIG. 25

Spatial Models, Total Wet Fallout (Rainout + Washout)

When considering the total amount of wet fallout ($mg/m^2/yr$) of an element or compound on a particular area, two interrelated parameters are of importance: the amount of precipitation and the ionic concentration in the rainwater. The discussion of the following maps of the seven chemicals being considered emphasizes the importance of total wet fallout information for ecosystem studies.

The stations used for the wet fallout maps (Figures 26-32) are listed in Table VI on page 31. All 35 stations were used where applicable, i.e. stations 30-33 did not have complete data and extrapolations were made by filling in the missing data, taking into account expected precipitation and elemental concentrations. Stations 34 and 35 were used according to the elements and compounds analyzed in those studies (WELLS, WHIGHAM & LIETH 1972; BEST 1971).

The seven total wet fallout maps are discussed on pages 48 - 61.

Summary of Rainout, Washout and Total Wet Fallout Information

Tables VII (opposite page) and VIII (page 62) summarize the information on rainout concentration, washout concentration, and total wet fallout. They give a tabular version of the points brought out in the mapping of the rainout, washout, and total wet fallout for the seven chemicals; and are meant to indicate the range of concentrations found for each of the seven chemicals in each of the four categories: coastal rural, coastal urban, continental rural, and continental urban. It was very difficult to find even two stations for each of the categories which showed the same trends for all the chemicals studied. The high degree of variability among the stations is probably caused by the local meteorological and physical conditions.

Table VII. Characteristic levels in $mg/m^2/yr$ of rainout (base level of elements or compounds in precipitation), washout and total wet fallout in precipitation for typical stations from four types of conditions: coastal rural, coastal urban, continental rural and continental urban.

		STATIONS							
		COASTAL				CONTINENTAL			
		RURAL		URBAN		RURAL		URBAN	
		1#	2	3	4	5	6	7	8
Ca^{++}	B	59*	95	161	24	122	121	407	624
	W	266	411	469	172	462	385	2242	2392
	T	325	506	630	196	584	506	2649	3016
K^+	B	86	121	86	16	14	39	60	80
	W	106	211	99	25	70	46	100	170
	T	192	332	185	41	84	85	160	250
Na^+	B	490	1361	86	73	16	35	61	113
	W	2377	2589	343	116	148	74	75	509
	T	2867	3950	429	189	164	109	136	622
Cl^-	B	882	2099	54	129	30	74	122	273
	W	3929	5586	915	581	202	70	195	1404
	T	4811	7685	969	710	232	144	317	1677
NH_4^+	B	62	90	96	7	5	15	20	27
	W	44	39	181	242	25	45	12	117
	T	106	129	277	249	30	60	32	144
NO_3^-	B	78	56	80	129	9	18	38	59
	W	401	330	429	1026	21	400	458	740
	T	479	386	509	1155	30	418	496	799
SO_4^{--}	B	294	594	4997	342	19	162	576	2198
	W	1598	1658	175	458	781	775	1505	5002
	T	1892	2252	5172	800	800	827	2081	7200

#Stations:
1 Nantuckett, Massachusetts
2 Cape Hatteras, North Carolina
3 Philadelphia, Pennsylvania
4 Los Angeles, California
5 Pocatello, Idaho
6 Grand Island, Nebraska
7 Columbia, Missouri
8 Chicago (Midway), Illinois

*For each station and element/compound, the 3 numbers refer to:
B = Base level ($mg/m^2/yr$)
W = Washout ($mg/m^2/yr$)
T = Total fallout ($mg/m^2/yr$)

Figure 26. Ca^{++} Total Wet Fallout Map.

The calcium fallout map emphasizes that oceanic areas have a lower yearly input of calcium than does the interior. The main source of calcium is continental aerosols; oceanic aerosols have a lower concentration for this element.

Exceptions to this trend are the Florida panhandle and Tatoosh, Washington. The high calcium input in the Florida panhandle is related to the calcium carbonate bedrock in this area. The high concentration of calcium fallout in the Tatoosh area is ascribed to the high yearly average rainfall (1075 mm). We see that a high fallout level can be caused by high precipitation as well as by high concentration in rainwater.

Industrial areas contribute significantly to calcium fallout, exemplified by the high yearly input around Chicago, Illinois; St. Louis, Missouri; Columbia, Missouri; and Albany, New York. These are areas where gypsum and other calcium-related materials are processed.

The low concentrations of calcium fallout along the midwestern U.S.-Canadian border are due, in part, to the low precipitation in this area, and to the low sources of the material, either natural or anthropogenic.

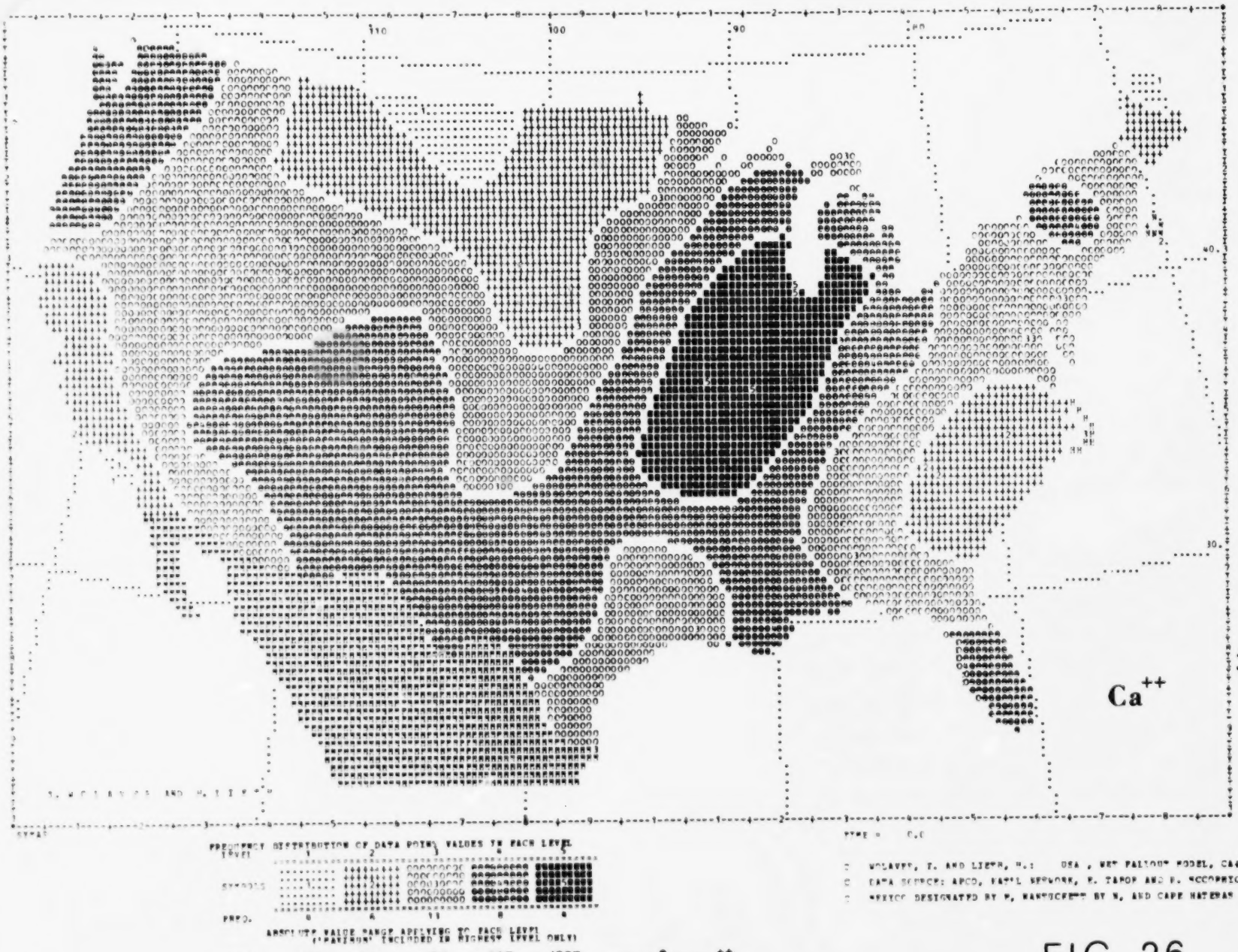

110
100
90
80
40.
30.
49
Ca^{++}
TYPE = C.C
FREQUENCY DISTRIBUTION OF DATA POINT VALUES TO EACH LEVEL
LEVEL
1
2
3
4
5
SYMBOLS
PROP.
0
6
11
17
ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
('PATTERN' ENCLOSED IN HIGHEST LEVEL ONLY)
MIN. 180 245 497 997 1997 MG/M²/YR(Ca^{++})
MAX. 245 497 997 1997 3407

FIG. 26

Figure 27. K^+ Total Wet Fallout Map.

The K^+ fallout map shows the effect of precipitation on total fallout. The potassium base level concentration from rainout is constant over the whole United States, while the washout concentration tends to show higher values throughout the dry areas of the Southwest. The total fallout map shows a reversal of the washout trend in that coastal areas tend to get a higher input than does the interior. The crucial factor is the increased rainfall in coastal areas, occasionally nine times that of the interior.

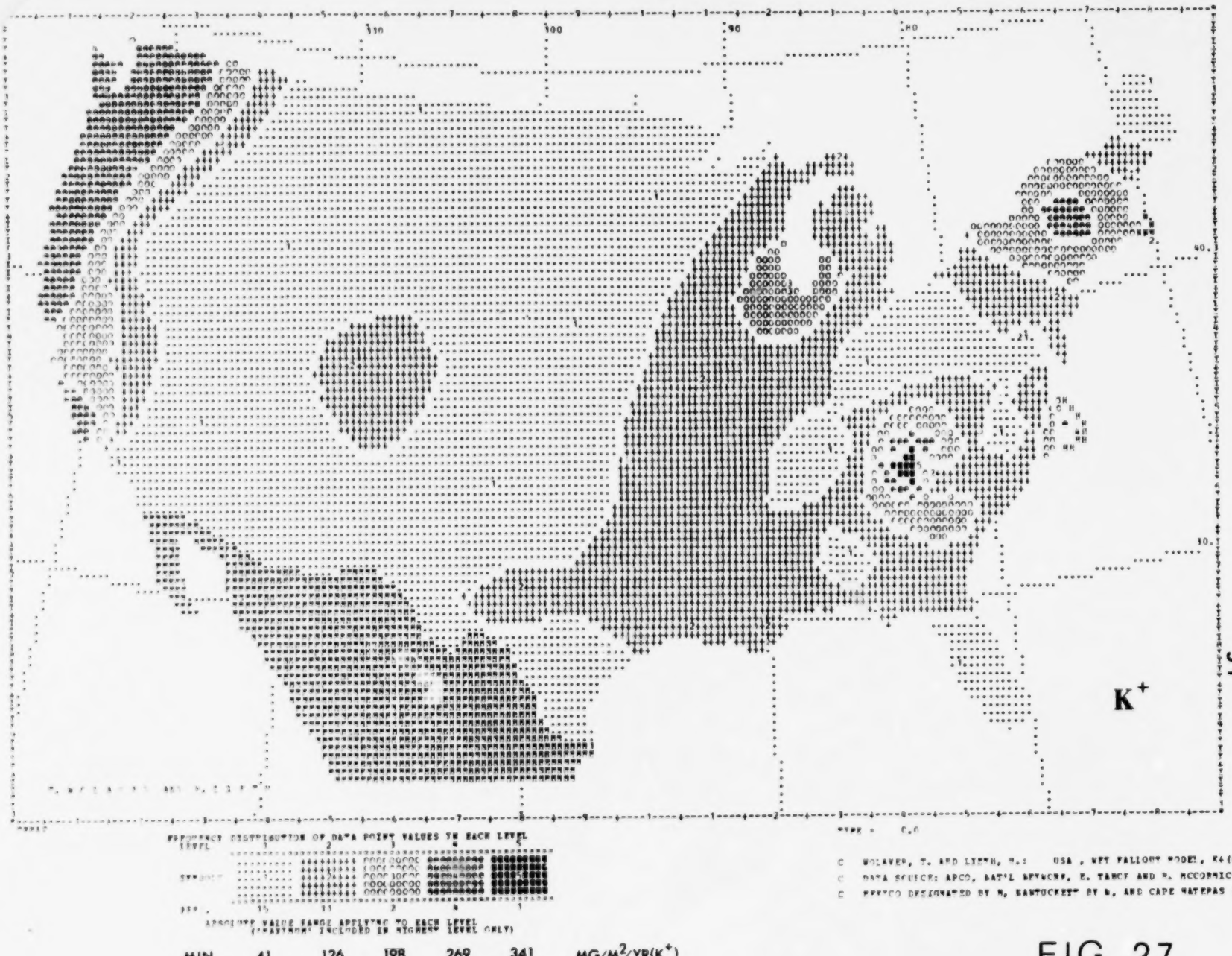


FIG. 27

Figure 28. Na^+ Total Wet Fallout Map.

The sodium fallout map illustrates the coupled effects of higher precipitation and oceanic aerosols laden with sodium. This produces a sodium fallout distribution map with high concentrations near coastal areas and lower values found toward the interior.

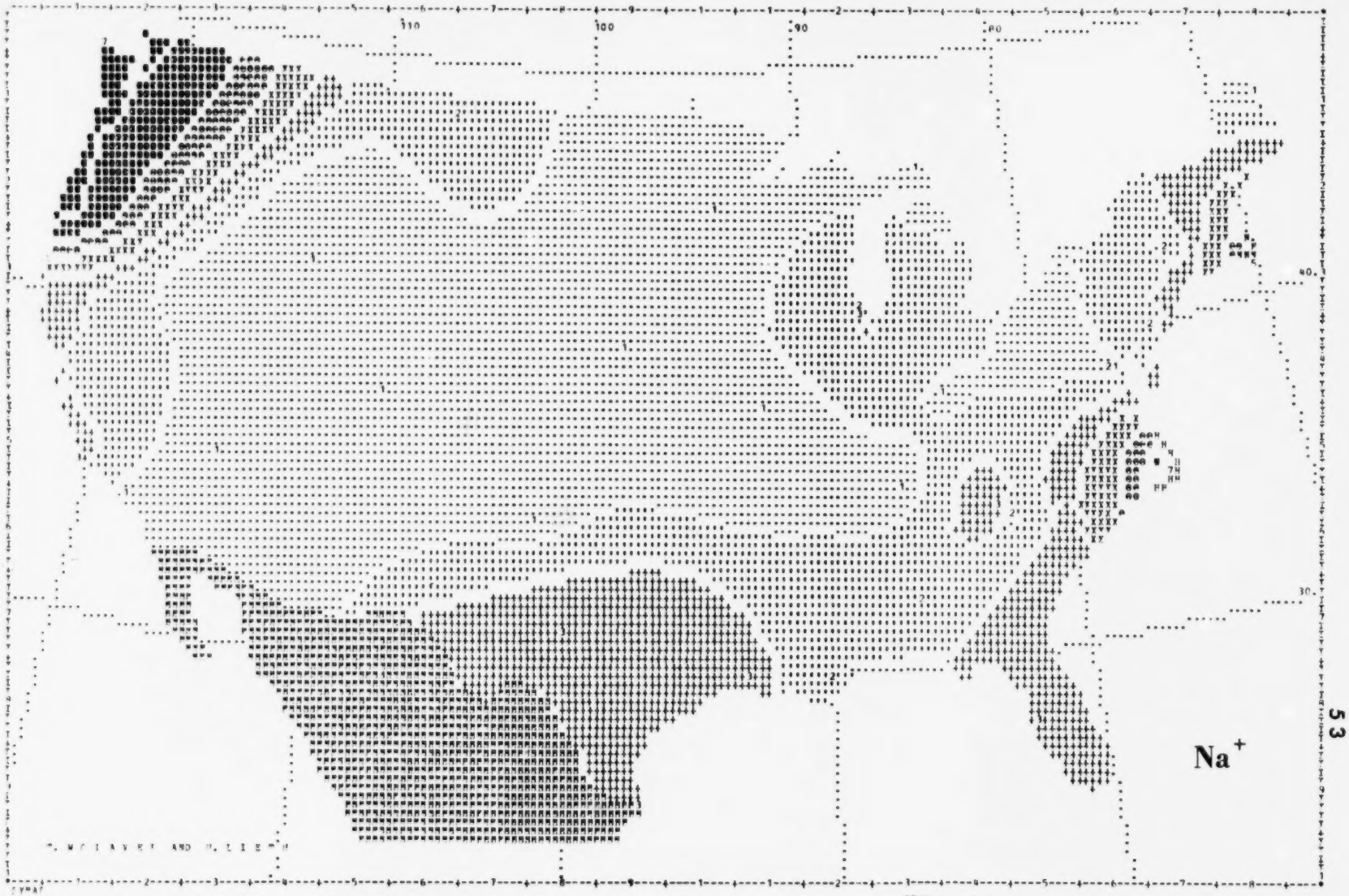
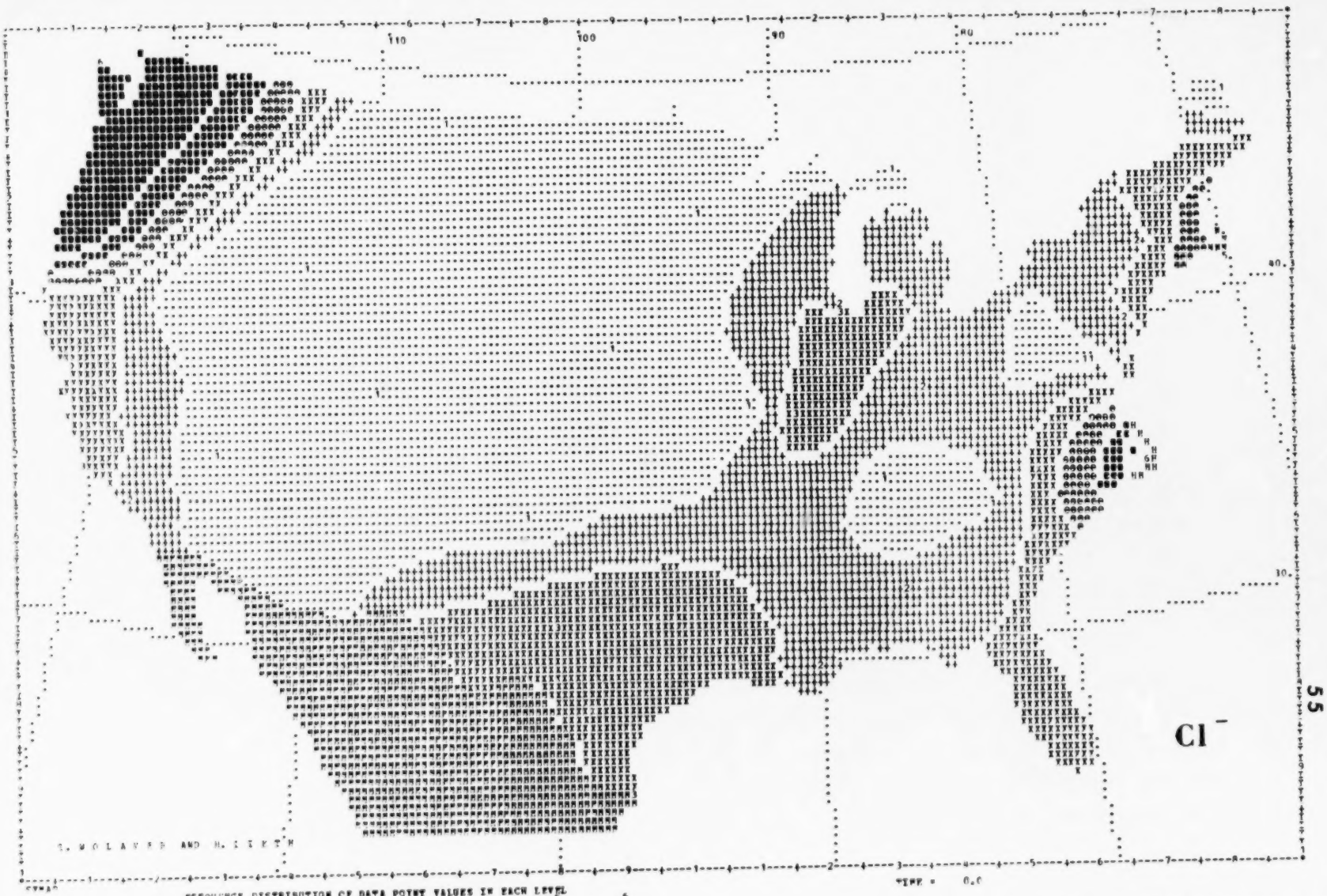

Na+
53
FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL
LEVEL 1 2 3 4 5 6 7
SYMBOLS
FREQ. 11 8 8 0 1 0 2
ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
("MAXIMUM" INCLUDED IN HIGHEST LEVEL ONLY)
MIN. 64 248 500 998 2006 3003 3573
MAX. 248 500 998 2006 3003 3573 4000
MG/M2/YR(Na+)
TYPE = 0.0
C MOHAVE, T. AND LIETH, H.: USA , WET FALLOUT MODEL, NA+ (MG/M2/.
C DATA SOURCE: APCO, NATL NETWORK, E. TABOR AND P. MCCORMICK
C MEXICO DESIGNATED BY M, NANTUCKETT BY N, AND CAPE HATTERAS BY H.

FIG. 28

Figure 29. Cl^- Total Wet Fallout Map.

The chlorine fallout distribution closely resembles that of sodium. This would be expected since sodium and chlorine have the same major source in oceanic aerosols. It is interesting to note that chlorine formed as a by-product of combustion seems to affect significantly the total fallout of this element around major industrial areas such as Chicago, Illinois, and St. Louis, Missouri.


Cl⁻
55
T. MOLAVEE AND H. LIETH
TIME = 0.0
C MOLAVEE, T. AND LIETH, H.: USA , WET FALLOUT MODEL, CL-(MG/M2/..
C DATA SOURCE: APCO, NATL NETWORK, E. TABOR AND P. MCCORMICK
C *EXTCO DESIGNATED BY M, NANTUCKET BY N, AND CAPE HATERAS BY P.

FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL

	1	2	3	4	5	6
SYMBOL	.	+	X	Y	H	@
FREQ.	14	7	8	0	1	2

ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
(*=MAXIMUM INCLUDED IN HIGHEST LEVEL ONLY)

MIN.	144	498	1000	1990	3993	5997	MG/M²/YR(Cl⁻)
MAX.	498	1000	1990	3993	5997	8000	

FIG. 29

Figure 30. NH_4^+ Total Wet Fallout Map.

The ammonium fallout map depicts the same trend as that for chlorine, indicating that similar processes may be affecting the large scale distribution of these two chemicals. Since we know that the ammonium base level concentration is constant throughout the United States, the difference in fallout concentration must be due to washout concentration and precipitation. We have no complete explanation for the ammonium fallout patterns.

In addition, point- and area-sources of ammonium are important, such as those around Los Angeles, Philadelphia, and areas in the uppermost northeastern section of the U.S. These point- and area-sources can be attributed to ammonia fertilizers (in the Los Angeles area) and release from combustion in urban areas such as Philadelphia, Sault Sainte Marie (near Detroit), and Los Angeles.

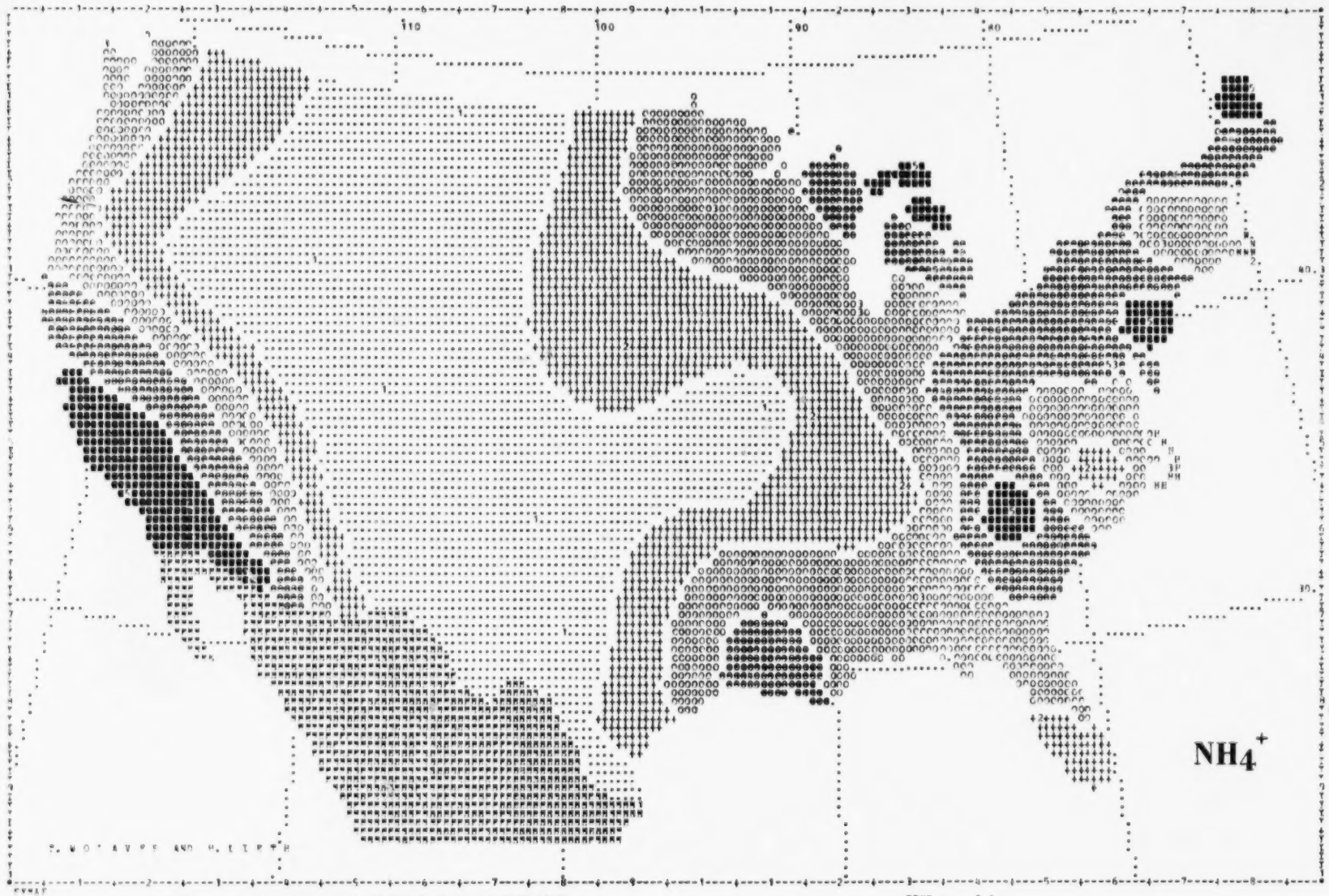

NH_4^+
57
FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL
LEVEL 1 2 3 4 5
FREQ. 6 7 8 3 6
ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
("MAXIMUM" INCLUDED IN HIGHEST LEVEL ONLY)
MIN. 30 52 107 161 215
MAX. 52 107 161 215 277
MG/M2/YR(NH4+)
C MCLAVEY, T. AND LYETH, H.: USA , WET FALLOUT MODEL, NH4+(PG/M2/..
C DATA SOURCE: APCO, NAPIL NETWORK, E. TABOR AND W. MCCORMICK
C MEXICO DESIGNATED BY T, MANHOCKET BY M, AND CAPE HATTERAS BY H.

FIG. 30

Figure 31. NO_3^- Total Wet Fallout Map.

The nitrate fallout map is similar to the nitrate washout map. This implies that point- and area-sources play a larger role in the total fallout distribution of this compound than do precipitation patterns. The nitrate fallout distribution is higher in the Southwest and Northeast. These higher values are due to industrial point- and area-sources in the Los Angeles area and in the industrial Northeast. The lower values throughout the Northwest and Southeast may be related to natural factors, either to low rainfall or possibly to soil-air interactions as explained in the discussion of the nitrate washout map (Figure 24).

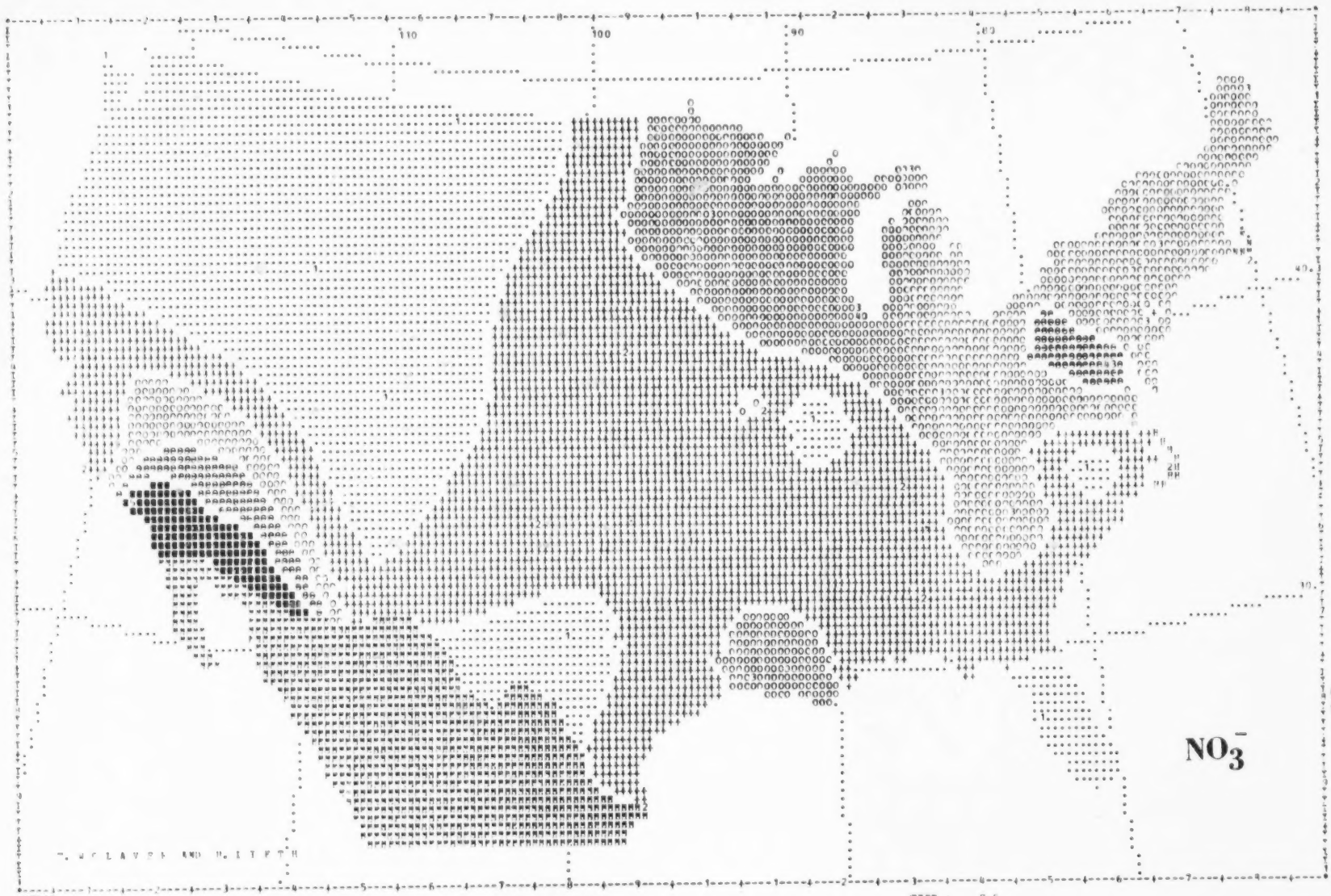

NO_3^-
59
FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL
LEVEL
SYMBOLS
FREQ.
ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
(MAXIMUM INCLUDED IN HIGHEST LEVEL ONLY)
MIN. 30 250 499 749 999 MG/M²/YR(NO_3^-)
MAX. 250 499 749 999 1156

FIG. 31

Figure 32. SO_4^{--} Total Wet Fallout Map.

The sulfate fallout distribution follows the trend of nitrate distribution. The major factors controlling the total fallout of this compound tend to be anthropogenic, even though natural sources can be quite important, as discussed in connection with the sulfate washout map (Figure 25).

The high values for sulfate occur in the industrial Northeast. The area of the United States west of Chicago has a uniformly low concentration, due to limited anthropogenic sources of this compound, and to low rainfall. An exception occurs in the area of Tatoosh, Washington, where extremely high precipitation values offset minimal urban sources to produce a fairly high fallout of sulfate.

It is interesting to note that the Los Angeles Basin does not appear to be an area of high sulfate fallout, even though there is a great deal of industry and population in this area. Discrepancies such as this should be examined further to find the specific sources of certain chemicals, and then to learn why the expected high fallout may not exist when known sources are present.

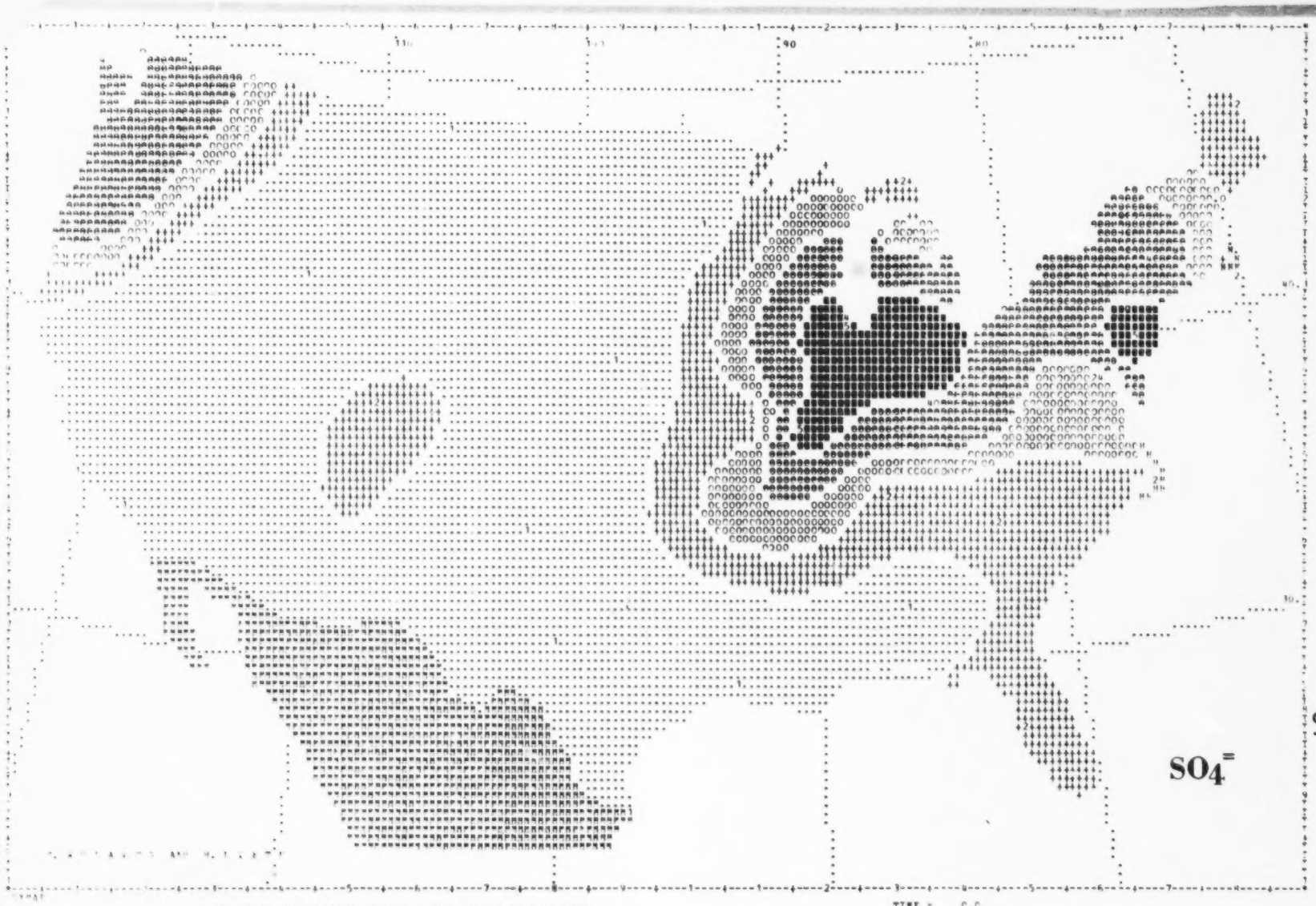

$SO_4^=$
61
FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL
LEVEL 1 2 3 4 5
SYMBOLS
FREQ. 11 11 0 5 1
ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
('MAXIMUM' INCLUDED IN HIGHEST LEVEL ONLY)
MIN. 700 1500 2501 3502 5003
MAX. 1500 2501 3502 5003 7200
MG/M2/YR(SO4=)
TIME = 0.0
C MOLAVER, Y. AND LIETH, H.: USA , WET FALLOUT MODEL, SO4(MG/M2/.
C DATA SOURCE: APCO, NAPAP NETWORK, P. TARCS AND R. MCCORMICK
C MEXICO DESIGNATED BY M, NANTUCKET BY N, AND CAPE HATTERAS BY H.

FIG. 32

Table VIII. Characteristic concentrations (ppm) for base level and washout for typical stations from four selected conditions: coastal rural, coastal urban, continental rural, and continental urban.

		STATIONS							
		COASTAL				CONTINENTAL			
		RURAL		URBAN		RURAL		URBAN	
		1#	2	3	4	5	6	7	8
Ca^{++}	B	.06 *	.075	.15	.1	.65	.26	.6	1.05
	W	.271	.323	.438	.705	2.47	.830	3.31	4.02
K^{+}	B	.088	.095	.08	.067	.075	.083	.089	.135
	W	.108	.166	.093	.117	.374	.099	.147	.286
Na^{+}	B	.5	1.07	.08	.3	.087	.074	.09	.19
	W	2.43	2.03	.321	.475	.791	.159	.111	.857
Cl^{-}	B	.9	1.65	.05	.53	.16	.16	.18	.46
	W	4.01	4.39	.855	2.38	1.08	.151	.288	2.36
NH_4^{+}	B	.072	.071	.09	.03	.028	.033	.03	.046
	W	.045	.031	.169	.992	.134	.097	.018	.197
NO_3^{-}	B	.08	.044	.075	.53	.047	.038	.056	.1
	W	.409	.259	.401	4.205	.112	.862	.675	1.25
SO_4^{--}	B	.3	.467	4.67	1.4	.1	.35	.85	3.7
	W	1.63	1.303	1.64	1.877	4.18	1.43	2.22	8.42

#Stations: 1 Nantuckett, Massachusetts
2 Cape Hatteras, North Carolina
3 Philadelphia, Pennsylvania
4 Los Angeles, California
5 Pocatello, Idaho
6 Grand Island, Nebraska
7 Columbia, Missouri
8 Chicago (Midway), Illinois

*For each station and element/compound, the two numbers refer to:

B = Base level (ppm)

W = Washout (ppm)

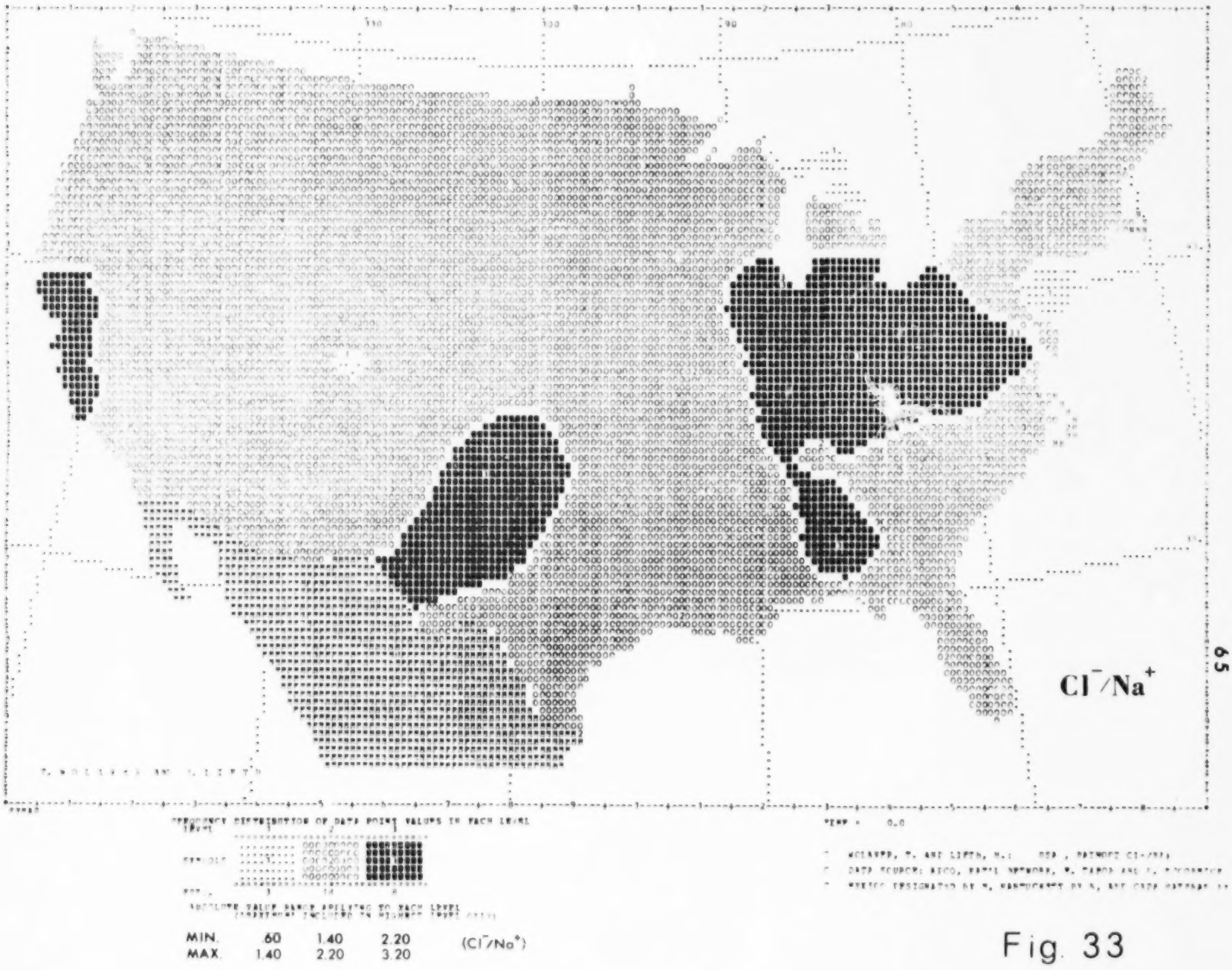
Spatial Models, Na^+/K^+ and Cl^-/Na^+ Concentration Ratios

To indicate chemical sources and to delineate air masses, Cl^-/Na^+ concentration ratios have been plotted for both Europe and the U.S. (JUNGE & WERBY 1958, JUNGE 1963, LODGE et al. 1968). Many processes have been hypothesized to explain the great variation in the Cl^-/Na^+ ratio (JUNGE 1963).

Our own studies indicate that the base level of individual elements may themselves suggest the origin of the air masses, according to their concentrations of certain elements. Therefore, we tried a combination of the two approaches, concentration ratio and rainout-washout discrimination, in an attempt to clarify the delineation of continental and marine air masses. Rainout and washout maps were produced for the concentration ratios of Na^+/K^+ and Cl^-/Na^+ across the U.S. (Figures 33-36).

Figure 33. Cl^-/Na^+ Rainout Map.

In executing the Cl^-/Na^+ rainout map, we allowed the Cl^-/Na^+ ratio to vary from 1.4 to 2.2 (centering around 1.8, the ratio of these elements in seawater). Most of the ratios found across the U.S. fell within this range. This implies that in both continental and marine air masses, excluding the effects of local intrusions, sea-salt aerosols are the predominant source of Na^+ and Cl^- in the rainout process. The high values for the ratio around Chicago and California are easily explained by the input of Cl^- from the combustion of fuels in urban areas. The other anomalies require further investigation. Compare this figure with Figure 35 of Na^+/K^+ rainout.



MIN.	.60	1.40	2.20	(Cl^-/Na^+)
MAX.	1.40	2.20	3.20	

Fig. 33

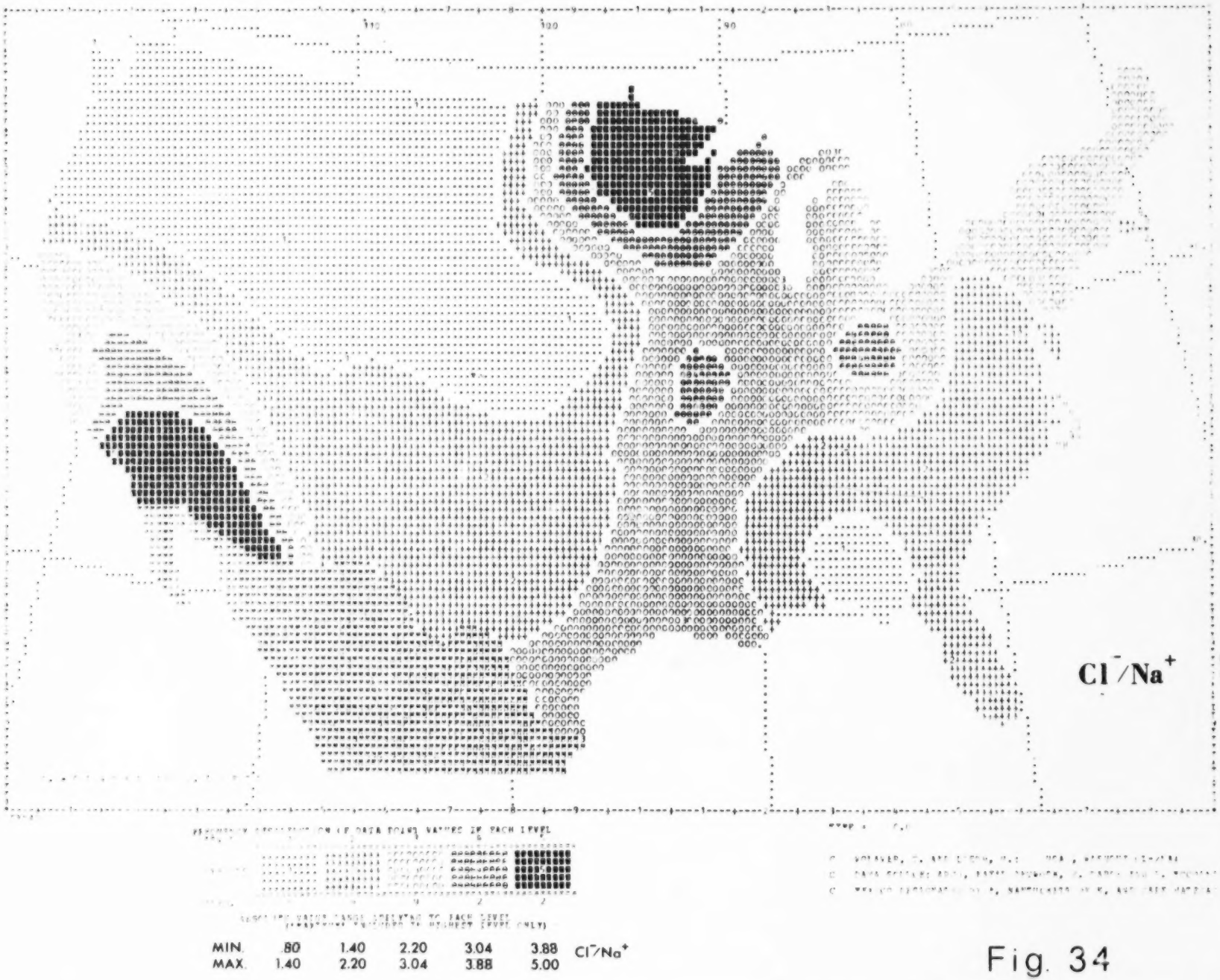
Figure 34. Cl^-/Na^+ Washout Map.

The washout map of Cl^-/Na^+ shows how the average ratio of 1.8 can be modified by local intrusions. The high values throughout the Northeast, sections of the Midwest, and southern California are probably due to the introduction of Cl^- from fuel combustion. The pattern of lower ratios through the Northwest requires a denser data base before a logical explanation may be attempted.

JUNGE (1963) indicates that Cl^-/Na^+ ratios in soil particles are generally lower than 1.8 because the concentration of Cl^- is lower than that of the alkali metals. ERIKSSON (1960) suggested another process which could lower the Cl^-/Na^+ ratio when he pointed out that organic films, which are found often on the sea's surface, may change the ratio of Cl^-/Na^+ by increasing the cation concentration of the surface water. None of these processes provide complete explanations for the low ratios, even though all may have an effect.

It can be assumed, then, that most continental and marine air masses should have a ratio of Cl^-/Na^+ similar to that of seawater, excluding the washout influence. If they do not, the major reason will be very heavy influxes of Cl^- or Na^+ affecting the rainout concentrations.

Compare this map with Figure 36 of Na^+/K^+ washout.



MIN.	.80	1.40	2.20	3.04	3.88	Cl^-/Na^+
MAX.	1.40	2.20	3.04	3.88	5.00	

Fig. 34

Figure 35. Na^+/K^+ Rainout Ratio.

The high values of the Na^+/K^+ ratio along the coastlines show the effect of Pacific, Caribbean and Atlantic influences. The values for much of the interior fall into the range of 0.81 - 1.32, closely corresponding to the average ratio by weight of Na^+ and K^+ in crystal rocks (1.1). This implies that the base level concentrations of continental air masses for K^+ and Na^+ are not affected by point- or area-sources, but reflect the average composition of the lithosphere for these two elements. It may be assumed that most marine air masses will have a ratio of Na^+/K^+ approximately that in seawater of 27.6.

The low ratio of Na^+/K^+ rainout in the Southwest coincides with a high value of Cl^-/Na^+ washout, shown in Figure 33. Otherwise, the patterns of the two maps appear contradictory for large parts of the interior in which the Cl^-/Na^+ washout suggests marine origin and the Na^+/K^+ rainout suggests continental sources for these elements.

While we may question the significance of these ratios for determining elemental origins and air mass patterns, the density of stations used for this study is limiting to such a degree that final conclusions are impossible.

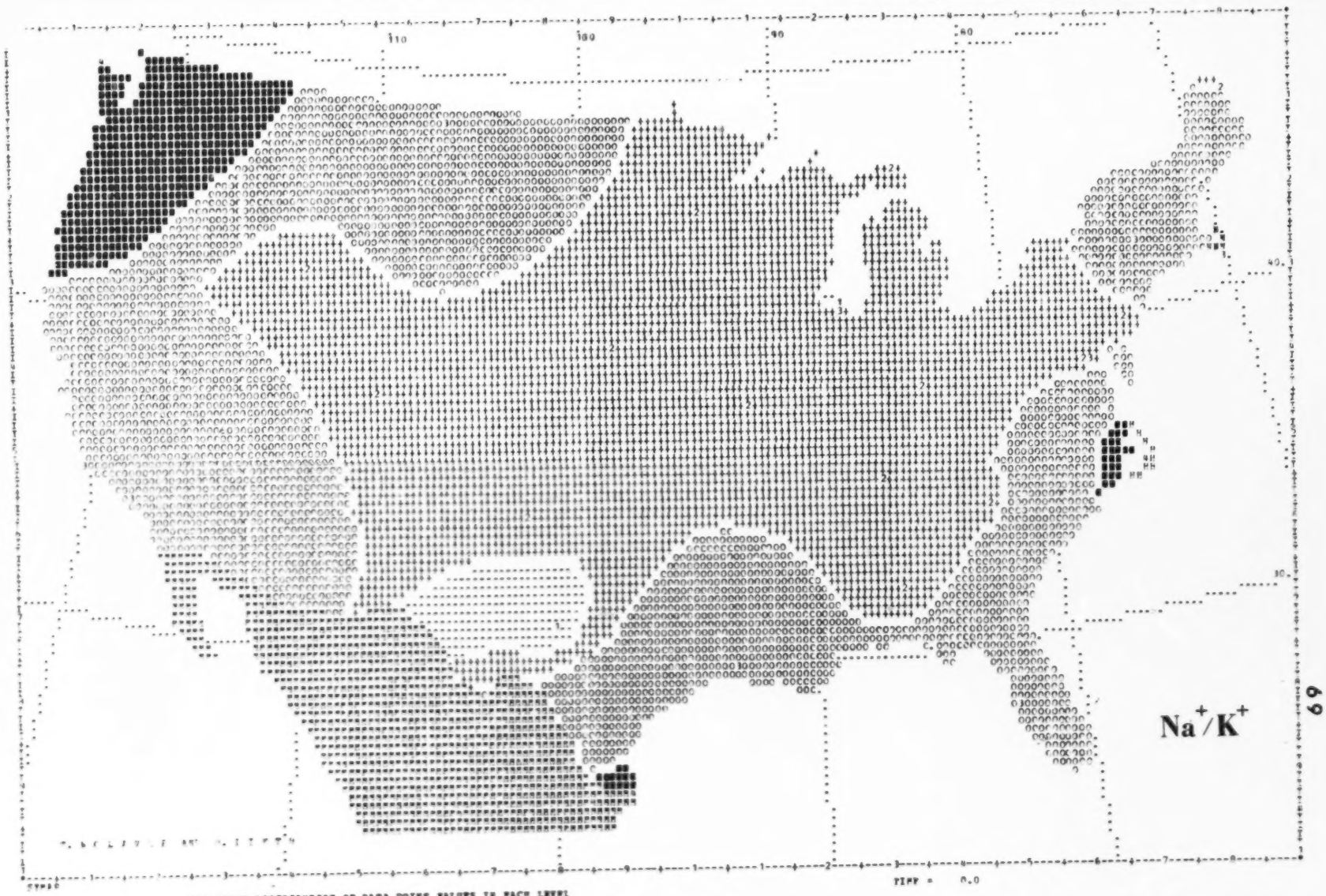

Na^+/K^+
FREQUENCY DISTRIBUTION OF DATA POINT VALUES IN EACH LEVEL
LEVEL
SYMBOL
FREQ.
ABSOLUTE VALUE RANGE APPLYING TO EACH LEVEL
MIN. .60 .81 1.32 5.82 Na^+/K^+
MAX. .81 1.32 5.82 15.60

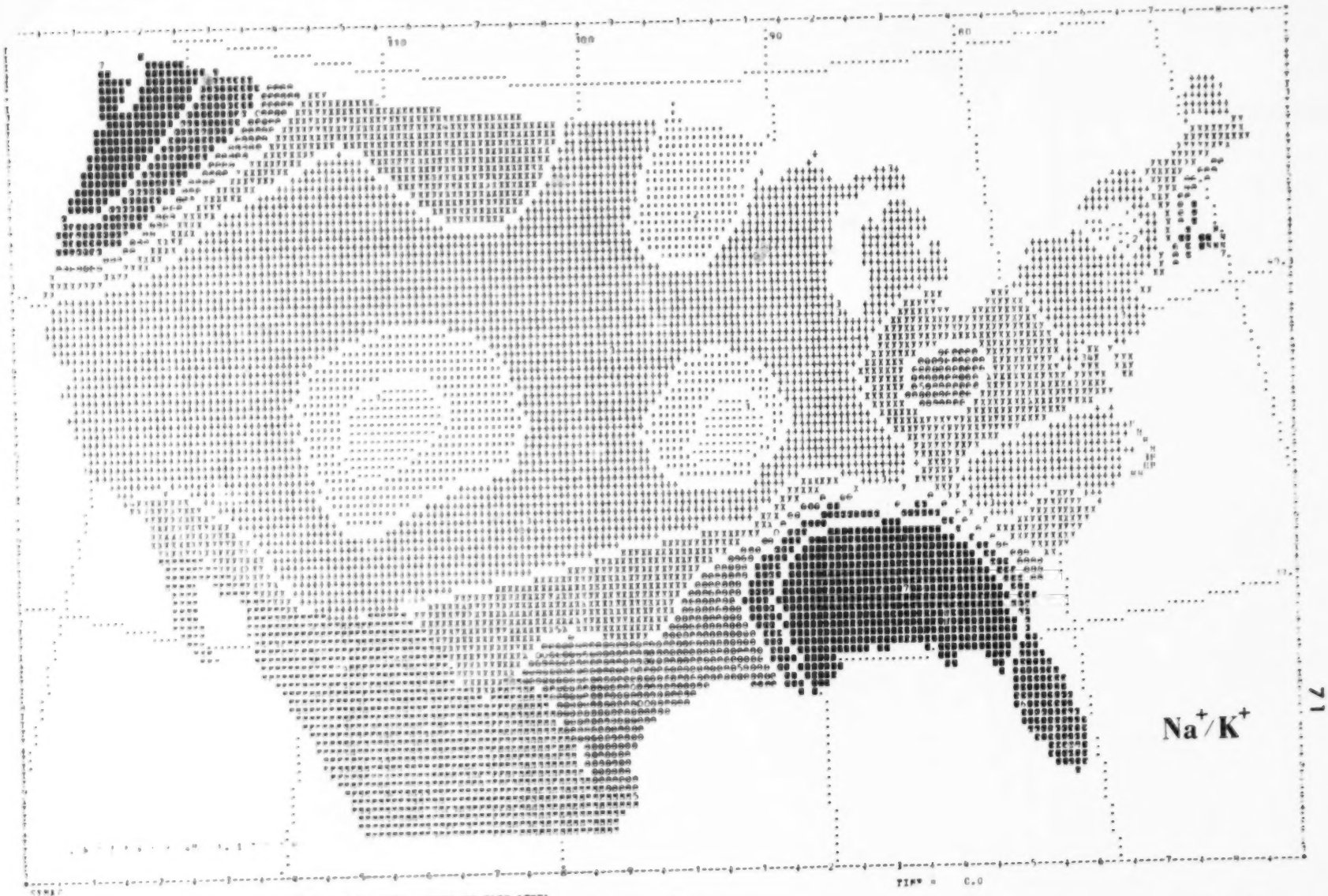
Fig. 35

Figure 36. Na^+/K^+ Washout Map.

The washout map of Na^+/K^+ indicates the source differences of the washout and rainout concentrations. Across most of the U.S., the washout process accounts for Na^+/K^+ ratios greater than 1.1. Local intrusions of continental aerosols and marine influences increase this ratio.

A comparison of Figures 34 and 36 is interesting in many respects. In several areas, maximum levels in Figure 34 coincide with minimum levels in Figure 36. The low density of stations probably accounts for a number of arbitrary delineations that may stem from the search-radius used in the SYMAP interpolation routine. While one may specify the size of the search-radius and the number of data points to be used in interpolation (READER et al. 1972, DUDNIK 1972), neither of these electives is very effective with only 33 data points for the entire U.S. Models of this kind certainly require a denser station network.

Additional difficulty in comparing the information in Figures 34 and 36 arises because they do not use the same mapping levels and the levels themselves are nonlinearly spaced.



MIN.	.60	.78	1.29	4.49	7.70	10.90	15.30
MAX.	.78	1.29	4.49	7.70	10.90	15.30	46.40

Na^+/K^+

Fig. 35

SUMMARY

This study has included the following:

1. A discussion of the negative exponential relationship between chemical concentration in rainwater vs. amount of precipitation. The general function was found to be $Y = U(1) \pm U(2)e^{\pm U(3)X}$, where Y is concentration in ppm, and X is amount of precipitation in mm (equation (1)). The characteristic curve (Figure 1) is a composite of the processes of washout, evaporation, dilution and rainout. PAGES 1-3.

2. An explanation of the method used to synthesize fallout information from all the stations for Ca^{++}, K^{+}, Na^{+}, Cl^{-}, NH_4^{+}, NO_3^{-}, and SO_4^{--}. The method is demonstrated with Figures 2-4. PAGES 3-5.

3. A method for separating total wet fallout data into rainout and washout components is given in equation (2). PAGES 5 & 6.

4. A table of partial correlation coefficients (Table I) was produced from data for 14 selected stations, to check for possible associations among the seven elements and compounds and pH. PAGES 6 & 7.

5. Four variations of the general function (Figure 5 and Table II) are presented: graphical model A for an area with moderate precipitation and natural chemical input; graphical model B&C for an area with high local intrusions of chemicals, natural or anthropogenic; graphical model D for an arid area with moderate chemical input, almost solely from washout; and graphical model E for an area of heavy precipitation and moderate chemical input, mostly from rainout. PAGES 8 & 9.

6. Using equation (1), quantitative models were derived for the synthesized concentration-vs.-precipitation curves for the chemicals under study, excluding SO_4^{--} (Figures 6-11 and Tables III & IV). The implications of the quantitative models are given, according to the implications of the graphical model they fit. PAGES 10-14.

7. Spatial models (contour maps) were produced for rainout, washout and total wet fallout concentrations of the chemicals studied. In addition to revealing areas of high and low concentration, these maps give some indication of the continental and marine air masses in the United States:

a. Table V shows probable chemical concentrations for continental and coastal air masses. This tentative information was used to evaluate the rainout maps (Figures 12-18). PAGES 15-29.

b. Table VI demonstrates that washout accounts for most of the annual chemical input. Maps of washout concentration are Figures 19-25. PAGES 32-45.

c. Maps of total wet fallout concentration are Figures 26-32. Tables VII & VIII summarize the rainout, washout and total wet fallout information shown in the maps. Eight stations were selected to show representative data from the following conditions: coastal rural, coastal urban, continental rural, and continental urban. PAGES 46-62.

8. The use of the Cl^-/Na^+ concentration ratio to delineate continental and marine air masses was tested. Maps of Cl^-/Na^+ and Na^+/K^+ concentration ratios in rainout and washout were made (Figures 33-36). Our results suggest that in both continental and marine air masses, the base level (rainout) concentration ratio of Cl^-/Na^+ approaches 1.8, as in seawater. Continental air masses are assumed to have a concentration ratio of Na^+/K^+ of about 1.1, as in crystal rock, while marine air will approach the concentration ratio in seawater of 26.4. Figures 33-36 of the Cl^-/Na^+ concentration ratios reveal more discrepancies than they provide conclusions. PAGES 63-71.

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